Inorg. Chem. **2007**, 46, 2870–2876

Inorganic Chemistry

Article

Complexation of U^{VI} with 1-Hydroxyethane-1,1-diphosphonic Acid in Acidic to Basic Solutions

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Received November 10, 2006

Complexation of U^{VI} with 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) in acidic to basic solutions has been studied with multiple techniques. A number of 1:1 (UO_2H_3L), 1:2 ($UO_2H_jL_2$ where $j = +4$, +3, +2, +1, 0, and –1), and 2:2 [$(UO_2)_2H_jL_2$ where $j = +1$, 0, and –1] complexes form, but the 1:2 complexes are the major species in a wide pH range. Thermodynamic parameters (formation constants and enthalpy and entropy of complexation) were determined by potentiometry and calorimetry. Data indicate that the complexation of U^{VI} with HEDPA is exothermic, favored by the enthalpy of complexation. This is in contrast to the complexation of U^{VI} with dicarboxylic acids in which the enthalpy term usually is unfavorable. Results from electrospray ionization mass spectrometry and ^{31}P NMR have confirmed the presence of 1:1, 1:2, and 2:2 U^{VI}HEDPA complexes.

1. Introduction

Complexation of diphosphonic acids with metal ions has been a subject of study because of its importance in biological, environmental, and separation processes. One of the most widely used diphosphonic acids is 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). This ligand has higher solubility in water than many other organodiphosphonic acids and forms strong complexes with many metal cations in acidic and basic solutions. As a result, it has found applications in therapeutic treatments as a bone calcium regulator,[1,2] in in vitro and vivo sequestration of uranium after contamination,[3,4] and in the treatment of nuclear wastes.[5−8] To understand the principles governing the behavior of metal ions and improve the efficiency of diphosphonic acids in these processes, it is necessary to identify the metal−ligand complexes and determine the thermodynamic parameters of the complexation.

One of the proposed strategies for the treatment of nuclear wastes on the Hanford site of the United States is to leach the waste sludge in the storage tanks with complexants such as HEDPA, prior to vitrification of the waste sludge.[5] The purpose of sludge leaching is to dissolve large quantities of nonradioactive components (e.g., aluminum) and small amounts of elements that are problematic to the vitrification (e.g., chromium), leaving most of the radioactive materials, especially the long-lived actinides, in the sludge that is subsequently vitrified. To evaluate the behavior of actinides in sludge leaching, the complexes of actinides with HEDPA must be identified and the thermodynamic parameters determined. In this work, we have studied the complexation of HEDPA with U^{VI}, the most abundant radioactive element in nuclear wastes and one of the radioactive environmental contaminants of greatest concern.

There have been a few studies on the complexation of HEDPA with f elements in acidic solutions, including U^{VI},[9,10]

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(1) Harris, S. T. *Osteoporosis Int.* **2001**, *12* (3), s11-6.
(2) Budavari, S., Ed. *Merck Index*, 11th ed.; Merck & Co.: Rahway, NJ, 1989; p 606.
(3) Tymen, H.; Hoffschir, D.; Gerasima, P.; Marty, J. P. *Ann. Pharm. Fr.* **2000**, *58*, 405.
(4) Tymen, H.; Gerasima, P.; Hoffschir, D. *Int. J. Radiat. Biol.* **2000**, *76*, 1417.
(5) Bond, A. H.; Nash, K. L.; Gelis, A. V.; Jensen, M. P.; Sullivan, J. C.; Rao, L. Scientific Basis for Nuclear Waste Management XXIII. *Mater. Res. Soc. Symp. Proc.* **2000**, *608*, 595.
(6) Nash, K. L.; Gelis, A. V.; Jensen, M. P.; Bond, A. H.; Sullivan, J. C.; Rao, L.; Garnov, A. Yu. *J. Nucl. Sci. Technol. Suppl.* **2002**, *3*, 512.
(7) Garnov, A. Yu.; Rao, L.; Nash, K. L.; Bond, A. H. *Sep. Sci. Technol.* **2003**, *38* (2), 359.
(8) Reed, W. R.; Garnov, A. Yu.; Rao, L.; Nash, K. L.; Bond, A. H. *Sep. Sci. Technol.* **2005**, *40* (5), 1029.
(9) Nash, K. L. *Radiochim. Acta* **1993**, *61*, 147.

10.1021/ic0621401 CCC: $37.00

Th^{IV},[11] and Eu^{III}.[12] With a solvent extraction method, Nash determined the stability constants ($\log \beta_{MH_jL_k}$) of two 1:1 U^{VI}-HEDPA complexes, UO_2H_3L (24.89) and $UO_2(H_3L)_2$ (49.81), and one 1:2 U^{VI}HEDPA complex, $UO_2H_4L_2$ (45.96), in strongly acidic solutions ($[H^+] = 0.01-0.1$ M, $I = 0.1$ M $NaClO_4$).[9,13] Using multiple spectroscopic techniques including electrospray ionization mass spectrometry (ESI-MS), NMR, and fluorescence spectroscopy, Jacopin et al. confirmed the stoichiometry of 1:1 and 1:2 U^{VI}HEDPA complexes and determined "conditional" stability constants in acidic solutions (pH up to 5.5).[10] Both studies[9,10] indicate that protonated U^{VI}HEDPA complexes form in acidic solutions and the 1:2 complexes are dominant in solutions when the ligand-to-metal ratio is equal to or above 2.

At present, there are no thermodynamic data in the literature on the complexation of U^{VI} with HEDPA in neutral to basic solutions, the conditions most relevant to the leaching of alkaline nuclear waste sludges such as those at the Hanford site. A study on the leaching of U^{VI} from the waste sludges has shown that a significant amount of U^{VI} could be leached by HEDPA or oxalic acid in a wide pH region (2−12).[7] The observation was interpreted as the result of the formation of complexes between U^{VI} and the complexants in acidic to basic solutions.[7] However, no thermodynamic data on HEDPA in neutral to basic solutions are available to support this interpretation. Therefore, the objective of the present study is to identify the U^{VI}HEDPA complexes that could form in the entire pH region (2−12) and obtain the thermodynamic properties of the complexation. Stability constants of the complexes as well as the enthalpy of complexation are determined by potentiometry and calorimetry. Optical absorption, ESI-MS, and NMR spectroscopy are used to help identify the stoichiometry of the complexes.

2. Experimental Section

2.1. Chemicals. All chemicals are reagent-grade or higher. All solutions were prepared with water of high purity from a Milli-Q system. The concentrations of U^{VI} and free acid in the stock solution were determined by absorption spectroscopy and fluorimetry[14] and Gran titration.[15] Tetramethylammonium chloride, $(CH_3)_4NCl$, was purified by recrystallization from ethanol. Tetramethylammonium hydroxide, $(CH_3)_4NOH$, was obtained as a 1 M solution, and the exact concentration was determined by Gran titration with standard HCl. HEDPA was obtained as a 60% solution and purified with glacial acetic acid by following a procedure in the literature.[12] The purity of the crystallized HEDPA product, $HEDPA{\cdot}H_2O(c)$, was confirmed by elemental analysis and NMR. The elemental analysis, used to check the percentage composition of C and H in the sample, showed good agreement between the expected and observed values: MW = 224; C, 10.71% (expected), 10.85% (observed); H, 4.46% (expected), 4.27% (observed). The ^1H NMR spectrum displayed a strong peak at approximately 21.5 ppm, indicative of HEDPA. The absence of a secondary peak (corresponding to the glacial acetic acid from which HEDPA was crystallized) confirmed the purity of the $HEDPA{\cdot}H_2O(c)$ solid. The above-mentioned chemicals were all purchased from Sigma-Aldrich.

Only the four protons of the phosphonate groups of HEDPA are dissociable in the pH region (1.5−12) of this study. As a result, HEDPA is denoted as H_4L in this paper, where L^{4-} represents the fully deprotonated HEDPA. All experiments were performed at 25 °C and an ionic strength of 1.0 M $(CH_3)_4NCl$. This ionic medium, instead of $NaClO_4$ or NaCl, was chosen for this study to eliminate complications from the ion pairing between Na^+ and the highly charged anionic species such as L^{4-}, $UO_2L_2^{6-}$, $UO_2HL_2^{5-}$, and $UO_2H_2L_2^{4-}$. Ion pairing between alkali cations and *gem*-diphosphonates has been well documented in the literature[16,17] and shown to cause errors in the determination of acid dissociation constants.[18] $(CH_3)_4NCl$ (1.0 M) was also chosen for the same reason as the ionic medium in a similar study of the complexation between U^{VI} and aminomethylenediphosphonates.[19] Precautions, including passing argon gas through or above the solutions, were taken to prevent the interference of carbon dioxide with the experiments at high pH.

2.2. Potentiometry. Potentiometric titrations were performed to determine the protonation constants of HEDPA and the stability constants of U^{VI}HEDPA complexes. Details of the titration setup and procedure have been given elsewhere.[20] In this work, the original inner solution of the glass electrode (3 M KCl) was replaced with 1 M sodium chloride to reduce the electrode junction potential.

The electrode potential (E, in millivolts) was measured with a Metrohm pH meter (model 713) equipped with a Ross combination pH electrode (Orion model 8102). In acidic and basic regions, E can be expressed by eqs 1 and 2, respectively, where R is the gas constant, F is the Faraday constant, and T is the temperature. K_w is the ionic product of water ($=[H^+][OH^-]$) and is equal to $10^{-13.94}$ in 1.0 M $(CH_3)_4NCl$.[21] The terms $\gamma_H[H^+]$ and $\gamma_{OH}[OH^-]$ are the electrode junction potentials for the hydrogen and hydroxide ions, respectively. Prior to each protonation or complexation titration, an acid/base titration with standard HCl and $(CH_3)_4NOH$ solutions was performed to obtain the electrode parameters of E^0, γ_H, and γ_{OH}. These parameters allowed the calculation of hydrogen ion concentrations from the electrode potential in the subsequent titration.

$$E = E^0 + RT/F \ln [H^+] + \gamma_H[H^+] \qquad (1)$$

$$E = E^0 + RT/F \ln K_w - RT/F \ln [OH^-] + \gamma_{OH}[OH^-] \qquad (2)$$

To determine the stability constants of U^{VI}HEDPA complexes, titrations were usually performed by titrating a solution containing U^{VI} and HEDPA ($C_{HEDPA}/C_U > 1$ and up to 4) with $(CH_3)_4NOH$. However, for the solutions with a lower ligand-to-metal ratio (e.g., $C_{HEDPA}/C_U = 1$), the titrations were exclusively carried out from the basic to acidic regions with HCl and terminated at $pC_H > 4$ ($pC_H = -\log [H^+]$) to avoid precipitation that could occur at $pC_H = 2-4$. Multiple titrations were conducted with solutions of different concentrations (C_{HEDPA}, C_H, and C_U). Approximately 75

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(10) Jacopin, C.; Sawicki, M.; Plancque, G.; Doizi, D.; Taran, F.; Ansoborlo, E.; Amekraz, B.; Moulin, C. *Inorg. Chem.* **2003**, *42*, 5015.
(11) Nash, K. L. *Radiochim. Acta* **1991**, *54*, 171.
(12) Nash, K. L.; Horwitz, E. P. *Inorg. Chim. Acta* **1990**, *169*, 245.
(13) Nash, K. L. *J. Alloys Compds.* **1997**, *249*, 33.
(14) Sill, C. W.; Peterson, H. E. *Anal. Chem.* **1947**, *19*, 646.
(15) Gran, G. *Analyst* **1952**, *77*, 661.
(16) Wada, H.; Fernando, Q. *Anal. Chem.* **1972**, *44*, 1640.
(17) Carroll, R. L.; Irani, R. R. *Inorg. Chem.* **1967**, *6*, 1994.
(18) Fonong, T.; Burton, D. J.; Pietrzyk, D. J. *Anal. Chem.* **1983**, *55*, 1089.
(19) Bollinger, J. E.; Roundhill, D. M. *Inorg. Chem.* **1994**, *33*, 6421.
(20) Jiang, J.; Rao, L.; Di Bernardo, P.; Zanonato, P.; Bismondo, A. *J. Chem. Soc., Dalton Trans.* **2002**, 1832.
(21) Martell, A. E.; Smith, R. M.; Motekaitis, R. J. *NIST Critically Selected Stability Constants of Metal Complexes Data Base*; NIST Standard Reference Database 46; U.S. Department of Commerce: Gaithersburg, MD, 1998.

Table 1. Protonation of HEDPA, $I = 1.0$ M $(CH_3)_4NCl$, $t = 25$ °C (the Error Limits Represent 3σ)

reaction	$\log \beta$	ΔG, kJ·mol^{-1}	ΔH, kJ·mol^{-1}	ΔS, J·K^{-1}·mol^{-1}
$H^+ + L^{4-} = HL^{3-}$	11.36(2)	−64.9(1)	−12.39(7)	176(1)
	11.14(5)[a]		−15.72(24)[b]	
$2H^+ + L^{4-} = H_2L^{2-}$	18.25(2)	−104.2(1)	−18.45(5)	288(1)
	18.07(5)[a]		−21.52(30)[b]	
$3H^+ + L^{4-} = H_3L^-$	20.88(3)	−119.2(2)	−16.21(9)	345(1)
	20.60(5)[a]		−17.26(34)[b]	
$4H^+ + L^{4-} = H_4L^0(aq)$	22.33(9)	−127.5(5)	−16.74(23)	371(2)
	22.03(5)[a]		−14.84(47)[b]	

[a] Reference 25. [b] Reference 26.

data points were collected in each titration. The protonation constants of HEDPA and the stability constants of U^{VI}HEDPA complexes were calculated using the program HyperQuad 2000.[22]

2.3. Calorimetry. Calorimetric titrations were carried out using an isoperibol solution calorimeter (ISC-4285; Calorimetry Sciences Corp., Lindon, UT). Descriptions of the calorimeter have been given elsewhere.[23] Three types of titrations were performed: (1) Acidic solutions containing U^{VI} and HEDPA ($C_{HEDPA}/C_U = 2$) were titrated with $(CH_3)_4NOH$ to p$C_H \sim 12$. (2) Basic solutions containing U^{VI} and HEDPA ($C_{HEDPA}/C_U = 1$) were titrated with HCl to p$C_H \sim 4$. (3) Acidic solutions containing only U^{VI} were titrated with HEDPA. The purpose of the third type of titration was to obtain enthalpy data for the $(UO_2)LH_3$ and $(UO_2)L_2H_4$ species that formed only in strongly acidic solutions. The pC_H value in these titrations was kept below 2 to ensure that no precipitation occurred.

For each titration, n experimental values of the total heat produced in the reaction vessel ($Q_{ex,j}$, where $j = 1$ to n, usually $n = 50-70$) were calculated as a function of the volume of the titrant added. These values were corrected for the heat of dilution of the titrant ($Q_{dil,j}$), which was determined in separate runs. The net reaction heat at the jth point ($Q_{r,j}$) was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. These data, in conjunction with the protonation and complexation constants obtained by potentiometry, were used to calculate the enthalpy of protonation and complexation with the computer program Letagrop.[24]

2.4. Absorption Spectroscopy. Absorption spectra of solutions containing U^{VI} and HEDPA at different acidities were collected from 350 to 550 nm on a Cary 5G spectrophotometer to identify the U^{VI}HEDPA complexes and obtain stability constants. A quartz cuvette of 1.0 cm optical length was used.

2.5. NMR. ^{31}P NMR experiments were performed using a JEOL FX90q FTNMR instrument. A series of D_2O solutions, containing 10 mM U^{VI} and 10 or 20 mM HEDPA, were prepared for the NMR experiments. The pH of the solutions was adjusted by adding $(CH_3)_4NOH$ or HCl to cover a wide region (1−13). ^{31}P NMR spectra were acquired using proton decoupling. All chemical shifts were measured with reference to a solution of phosphoric acid in D_2O. The samples were not spinned because vortexing in the tube decreased the resolution. The optimum time for pulse relaxation was found to be 15 s by using a 1D−2D technique.

2.6. ESI-MS. ESI-MS experiments were conducted on a Quattro mass spectrometer (Micromass, Berks, U.K.) to help identify the U^{VI}HEDPA complex species in solution. Experimental parameters were identical with those reported in the literature on the U^{VI}-HEDPA system.[10] Solutions containing $UO_2(ClO_4)_2$ (5×10^{-4} M) and HEDPA (1×10^{-3} M) were prepared for the experiments. The acidity of the solutions was adjusted by $(CH_3)_4NOH$ and HCl.

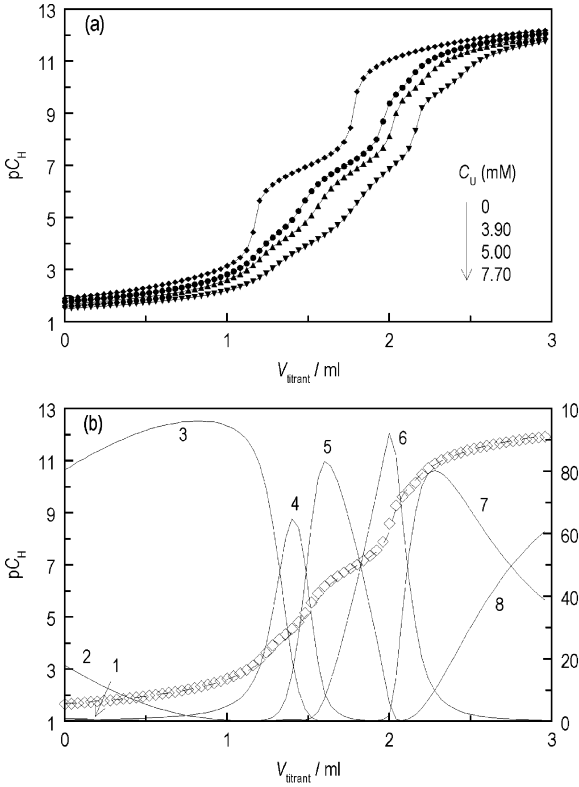

Figure 1. Potentiometric titration of U^{VI}HEDPA complexation, $I = 1.0$ M $(CH_3)_4NCl$, $t = 25$ °C, $V^0 = 40.0$ mL, titrant 1.014 M $(CH_3)_4NOH$. (a) $C^0_{HEDPA} = 15.20$ mM; $C^0_H = 60-65$ mM; $C^0_U = 0-7.70$ mM. (b) $C^0_{HEDPA} = 15.20$ mM; $C^0_H = 61.8$ mM; $C^0_U = 3.90$ mM. (◇) Experimental pC_H, left y axis. (dashed line) Calculated pC_H, left y axis. (solid lines) Percentages of U^{VI} species, right y axis. 1: UO_2^{2+}. 2: $UO_2H_3L^+$. 3: $UO_2H_4L_2^{2-}$. 4: $UO_2H_3L_2^{3-}$. 5: $UO_2H_2L_2^{4-}$. 6: $UO_2HL_2^{5-}$. 7: $UO_2L_2^{6-}$. 8: $UO_2(OH)L_2^{7-}$.

3. Results and Discussion

3.1. Protonation of HEDPA. The protonation constants and enthalpies are shown in Table 1. The protonation constants from this work are in good agreement with previous values obtained in the same ionic media [1 M $(CH_3)_4NCl$].[25] The enthalpies of protonation indicate that, stepwise, the first two steps of protonation are exothermic while the third and fourth steps are slightly endothermic or have near-zero enthalpy. Similar trends of stepwise enthalpy of the protonation of HEDPA are observed in 2 M $NaClO_4$.[26] The first two steps are favored by both enthalpy and entropy, while the last two steps are essentially entropy-driven.

3.2. Stability Constants of U^{VI}HEDPA Complexes. 3.2.1. Potentiometry. It is expected that HEDPA, like other diphosphonic acids,[9,10,13] could form a variety of complexes with U^{VI}, including the protonated complexes MH_jL_k in acidic solutions and the mixed hydroxyl complexes, $M(OH)_jL_k$ or $MH_{-j}L_k$, in basic solutions. Besides, polynuclear species could form when the ligand-to-metal ratio is low. To obtain stability constants for such a large number of complexes, it is necessary to perform multiple titrations with different

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(22) Gans, P.; Sabatini, A.; Vacca, A. *Talanta* **1996**, *43*, 1739.

(23) Rao, L.; Garnov, A. Yu.; Jiang, J.; Di Bernardo, P.; Zanonato, P.; Bismondo, A. *Inorg. Chem.* **2003**, *42* (11), 3685.

(24) Arnek, R. *Ark. Kemi* **1970**, *32*, 81.

(25) Kaila, L. Ph.D. Thesis (Oulu University, Oulu, Finland). *Ann. Acad. Sci. Fenn., Ser. A2* **1993**, *247*, 1.

(26) Nash, K. L.; Rao, L.; Choppin, G. R. *Inorg. Chem.* **1995**, *34*, 2753.

Table 2. Complexation of U^{VI} with HEDPA, $I = 1.0$ M $(CH_3)_4NCl$, $t = 25$ °C (the Error Limits Represent 3σ)

$M_iH_jL_k$							
i	j	k	reaction	log β	ΔG, kJ·mol^{-1}	ΔH, kJ·mol^{-1}	ΔS, J·K^{-1}·mol^{-1}
1	3	1	$UO_2^{2+} + 3H^+ + L^{4-} = UO_2H_3L^+$	24.43(16), 24.89[a]	−139.5(9)	−42.6(6)	325(4)
1	4	2	$UO_2^{2+} + 4H^+ + 2L^{4-} = UO_2H_4L_2^{2-}$	44.90(27), 45.10(24),[b] 45.96[a]	−256.3(15)	−87.5(18)	566(8)
1	3	2	$UO_2^{2+} + 3H^+ + 2L^{4-} = UO_2H_3L_2^{3-}$	41.00(5), 40.83(16)[b]	−234.1(3)	−82.3(13)	509(5)
1	2	2	$UO_2^{2+} + 2H^+ + 2L^{4-} = UO_2H_2L_2^{4-}$	35.94(5)	−205.2(3)	−85.1(11)	403(4)
1	1	2	$UO_2^{2+} + H^+ + 2L^{4-} = UO_2HL_2^{5-}$	28.87(5)	−164.8(3)	−81.2(11)	280(4)
1	0	2	$UO_2^{2+} + 2L^{4-} = UO_2L_2^{6-}$	18.93(6)	−108.1(3)	−67.7(12)	135(4)
1	−1	2	$UO_2^{2+} + 2L^{4-} + H_2O = UO_2(OH)L_2^{7-} + H^+$	7.17(8)	−40.9(5)	−33.0(14)	27(5)
2	1	2	$2UO_2^{2+} + H^+ + 2L^{4-} = (UO_2)_2HL_2^{3-}$	33.70(16)	−192.4(9)	−91.7(57)	338(19)
2	0	2	$2UO_2^{2+} + 2L^{4-} = (UO_2)_2L_2^{4-}$	24.03(20)	−137.2(11)	−87.9(45)	165(16)
2	−1	2	$2UO_2^{2+} + 2L^{4-} + H_2O = (UO_2)_2(OH)L_2^{5-} + H^+$	12.92(21)	−73.8(12)	−61.8(48)	40(17)

[a] Reference 13. $I = 0.1$ M. [b] Values obtained by spectrophotometric titrations in this work.

conditions. In this work, a total of 13 potentiometric titrations with varying concentrations of U^{VI}, HEDPA, and H^+ have been conducted. Analysis of all of the titrations was performed with HyperQuad 2000[22] to obtain the stability constants of the complexes. Figure 1a shows four titration curves for solutions with different ratios of C_{HEDPA}/C_U. Figure 1b shows the fitting of a representative titration (experimental and calculated pC_H), as well as the percentages of U^{VI} species in the titration. As shown in the figure, the dominant complexes were the 1:2 (M/L) species MH_jL_2, where j decreased from +4 to −1 as pC_H was increased from below 2 to 12 in the titration. The calculated stability constants of the U^{VI}HEDPA complexes are summarized in Table 2. Only the first two protonated complexes, MH_3L and MH_4L_2, have been identified in a previous study of strongly acidic solutions.[13] The stability constants of MH_3L and MH_4L_2 from the present study are in good agreement with those in the literature.[13] The other complexes MH_jL_2, where $j = +3$, +2, +1, 0, and −1, have not been observed in previous studies because they form only in weakly acidic to basic solutions. The stability constants for these complexes in Table 2 are the first such data that have been experimentally determined.

3.2.2. Absorption Spectroscopy. Two types of spectrophotometric titrations were performed to provide further information on the complexation of U^{VI} with HEDPA: (1) Solutions containing U^{VI} and HEDPA ($C_L/C_U \sim 1.8-2.5$) were titrated with $(CH_3)_4NOH$ or HCl. (2) Solutions of U^{VI} were titrated with HEDPA. Generally, the absorption bands of free UO_2^{2+} around 414 nm are red-shifted, and the intensities increased because of the formation of complexes with HEDPA. Most attempts to calculate the stability constants of U^{VI}HEDPA complexes from the spectrophotometric titrations were unsuccessful, probably because a large number of species (MH_jL_k) form (Table 2) and the changes in the absorption spectra are subtle. However, in a few titrations where only a limited number of U^{VI}HEDPA species were dominant, we were able to calculate the stability constants from the spectrophotometric titration data. Figure 2 shows the results of one representative titration. A speciation diagram (Figure 2a), calculated with the stability constants obtained by potentiometry (Table 2), shows that there are only two dominant complexes, $UO_2H_4L_2^{2-}$ and $UO_2H_3L_2^{3-}$, in this titration. Calculations with the HyperQuad program indicate that, indeed, $UO_2H_4L_2^{2-}$ and $UO_2H_3L_2^{3-}$ are the only two complexes that are necessary to fit the spectra (Figure 2b). Calculated absorption spectra of $UO_2H_4L_2^{2-}$ and $UO_2H_3L_2^{3-}$ as well as free UO_2^{2+} are shown in Figure 2c. The stability constants (log $\beta_{MH_jL_k}$) obtained by spectrophotometric titrations are 40.83 ± 0.16 for $UO_2H_3L_2^{3-}$ and 45.10 ± 0.24 for $UO_2H_4L_2^{2-}$. These values are in excellent agreement with those obtained by potentiometry (Table 2).

3.3. Enthalpy of Complexation. Experimental data of a calorimetric titration are shown in Figure 3, in the form of the total reaction heat, Q_r, and pC_H as a function of the titrant volume added. The distribution of U^{VI} species in the calorimetric titration is not shown in Figure 3 but is similar to that in the potentiometric titration shown in Figure 1b (the two titrations cover the same region of pC_H). A total of nine calorimetric titrations were performed, covering the formation of all of the U^{VI}HEDPA complexes identified by potentiometry. These data were used, in conjunction with the protonation constants and enthalpy of HEDPA and the stability constants of U^{VI}HEDPA complexes, to calculate the enthalpies of complexation. The values of enthalpy as well as entropy are summarized in Table 2. Using the enthalpies and formation constants in Table 2, a curve simulating the calorimetric titration was calculated and shown in Figure 3 (the dashed line). The good agreement between the curve and the experimental points confirms the mutual consistency of the calorimetric and potentiometric data on the complexation (Table 2) as well as the reliability of the data on the protonation of HEDPA (Table 1).

Comparison of the enthalpy and entropy data between phosphonic acids and carboxylic acids could provide insight into the energetics of complexation and the nature of the complexes. Figure 4 shows three structurally related ligands, including the H_2L^{2-} form of HEDPA, the HL^{2-} form of phosphonoacetic acid (PAA), and the L^{2-} form of malonic acid (MA). The stability constants of the 1:2 complexes between U^{VI} and the three ligands are comparable (log $\beta \sim 9-11$),[13,27] but the enthalpy and entropy of complexation for U^{VI}HEDPA are drastically different from those for U^{VI}MA. The enthalpy and entropy of complexation for the 1:2 complexes with MA ($UO_2^{2+} + 2L^{2-} = UO_2L_2^{2-}$) are both positive: $\Delta H = 11$ kJ·mol^{-1} and $\Delta S = 218$ J·K^{-1}·mol^{-1},[27] consistent with the formation of inner-sphere complexes

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(27) Rao, L.; Jiang, J.; Zanonato, P.; Di Bernardo, P.; Bismondo, A.; Garnov, A. Yu. *Radiochim. Acta* **2002**, *90*, 581.

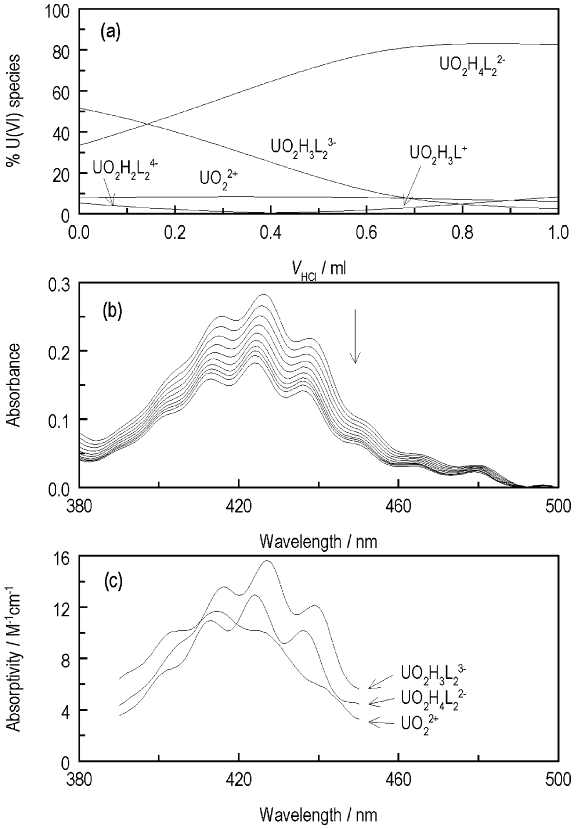

Figure 2. Spectrophotometric titrations, $I = 1.0$ M $(CH_3)_4NCl$, $t = 25$ °C. Initial solution: 2.5 mL, $C_U = 0.020$ M, $C_{HEDPA} = 0.0367$ M, $C_H = 0.0592$ M; titrant 0.0499 M HCl. (a) Speciation of U^{VI} in the titration calculated by the stability constants obtained by potentiometry (Table 2). (b) Absorption spectra (20 additions of 50 μL titrant per addition; the number of spectra is reduced for clarity). (c) Calculated molar absorptivities of UO_2^{2+}, $UO_2H_4L_2^{2-}$, and $UO_2H_3L_2^{3-}$.

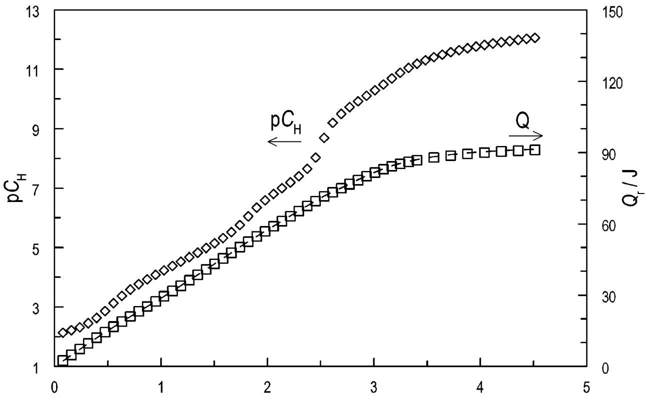

Figure 3. Calorimetric titration of U^{VI}HEDPA complexation, $I = 1.0$ M $(CH_3)_4NCl$, $t = 25$ °C. Cup: 20.0 mL, $C_H = 81.21$ mM, $C_U = 16.72$ mM, $C_{HEDPA} = 34.26$ mM; titrant 0.508 M $(CH_3)_4NOH$. Symbols: (◇) pC_H; (□) experimental heat of reaction (Q_r) in joules, (dashed line) calculated heat of reaction.

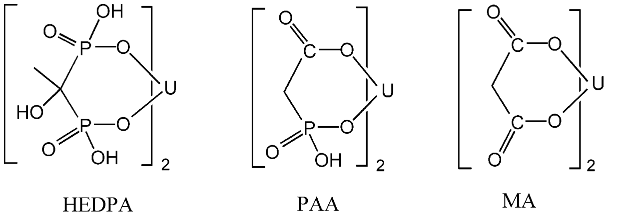

Figure 4. Comparison between the 1:2 U^{VI} complexes with HEDPA, PAA, and MA.

between hard acid and hard base.[28] The positive enthalpy and entropy values for uranium(VI) malonate complexation can be interpreted as due to the strong contribution of dehydration of the interacting cation and anion.[29] The energy required to dehydrate UO_2^{2+} and MA (L^{2-}) exceeds the energy released when UO_2^{2+} and L^{2-} combines, resulting in a positive enthalpy. The large positive entropy essentially reflects the increase in disorder when a number of water molecules are released from UO_2^{2+} and L^{2-}. On the contrary, the enthalpy of complexation for the 1:2 complexes with HEDPA ($UO_2^{2+} + 2H_2L^{2-} = UO_2H_4L_2^{2-}$) is negative, $\Delta H = -(50.6 \pm 1.8)$ kJ·mol^{-1}, and the entropy is near zero, $\Delta S = -(10 \pm 8)$ J·K^{-1}·mol^{-1} (from data in Tables 1 and 2; calculated from the parameters for the reaction $UO_2^{2+} + 4H^+ + 2L^{4-} = UO_2H_4L_2^{2-}$ in Table 2 and the parameters for the reaction $2H^+ + L^{4-} = H_2L^{2-}$ in Table 1). Large negative enthalpy and small entropy are usually associated with the formation of outer-sphere complexes where the energy released from the cation + ligand interaction exceeds the dehydration energy and the ordering of ionic charges (cation + ligand) is not accompanied by a compensatory disordering of the hydration sphere.[28] However, a previous fluorescence study on the complexation of Eu^{III} with HEDPA has shown that the $Eu(H_3L)_2$ complex is inner-sphere, despite the fact that the enthalpy of complexation is negative [$\Delta H = -(14.55 \pm 1.12)$ kJ·mol^{-1}] and the entropy is near zero ($\Delta S = 6 \pm 5$ J·K^{-1}·mol^{-1}).[26] The large negative enthalpy and small entropy are interpreted as the result of extensive intramolecular−interligand hydrogen bonding in the $Eu(H_3L)_2$ complex. Because the phosphonate groups in HEDPA are extensively protonated in the complex, many opportunities for solvent−complex hydrogen bonding exist. The formation of an extensive network of hydrogen bonds would lead to a more exothermic enthalpy of complexation, and a smaller entropy of complexation because the complex is highly ordered and additional ordering of water molecules in the secondary coordination sphere could occur.[13,26] On the basis of the experimental evidence and discussions for $Eu(H_3L)_2$, we assume that $UO_2H_4L_2^{2-}$ is also an inner-sphere complex and the large negative enthalpy and small entropy of complexation should be accounted for by the extensive hydrogen bonding in the protonated complex.

Comparison of the data for U^{VI}HEDPA and U^{VI}MA with those for the complexation of U^{VI} with PAA (Figure 4) could be particularly interesting because PAA has one phosphonate group and one carboxylate group. However, the enthalpy and entropy data for U^{VI}PAA are not available. We expect that the values for U^{VI}PAA are likely to be intermediate between those for the HEDPA and MA systems. A future study on the thermodynamic properties of U^{VI}PAA is planned.

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[28] Rizkalla, E. N.; Choppin, G. R. Lanthanides and Actinides Hydration and Hydrolysis. In *Handbook on the Physics and Chemistry of Rare Earths, Vol. 18—Lanthanides/Actinides: Chemistry*; Gschneider, K. A., Eyring, L., Jr., Choppin, G. R., Lander, G. H., Eds.; Elsevier Science BV: New York, 1994; p 572.

[29] Nancollas, G. H. *Interactions in Electrolyte Solutions*; Elsevier: Amsterdam, The Netherlands, 1966; pp 133−140.

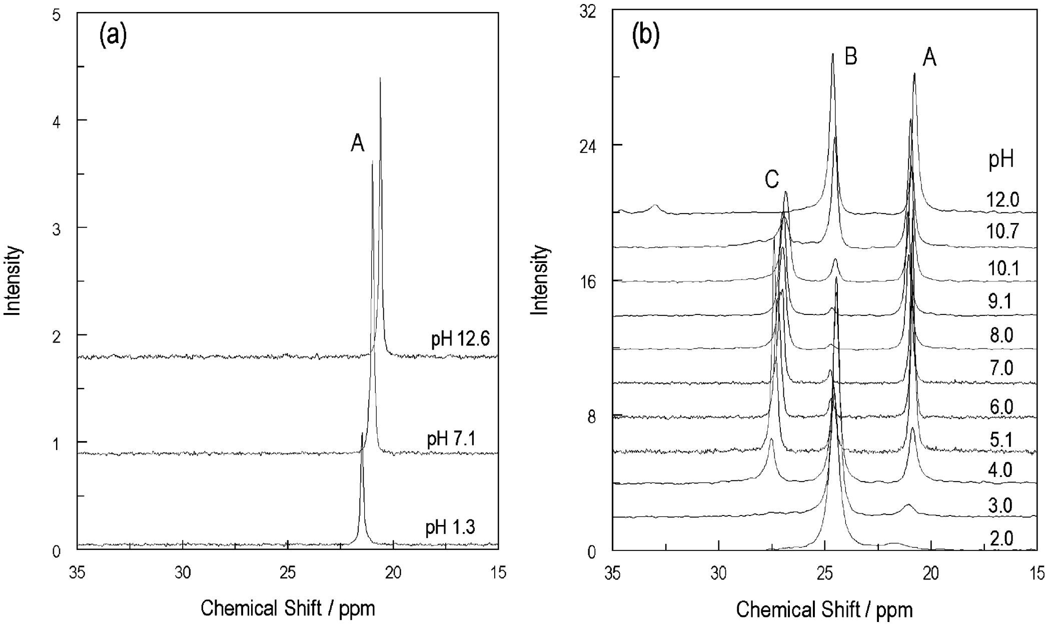

Figure 5. $^{31}P\{^1H\}$ NMR spectra: (a) 40.0 mM HEDPA; (b) 10.12 mM U^{VI}, 20.0 mM HEDPA, $pH_{obs} = 2-12$.

3.4. Characterization of Complexes. 3.4.1. ESI-MS. Acidic solutions containing U^{VI} and HEDPA were investigated in both positive and negative ionization modes. A number of cluster complexes containing uranyl and HEDPA as well as H_2O and $HClO_4$ were identified. For solutions of pH 2−7, 1:1 (MH_jL) and 1:2 (MH_jL_2) complexes with different numbers of H_2O and $HClO_4$ are the major species observed. Table S1 in the Supporting Information shows the *m*/*z* peaks for a solution of pH 2 in both positive and negative ionization modes and the peak assignments. In the positive mode, MH_3L species are observed at *m*/*z* 475.1 as $(UO_2)(H_3L)^+$, at *m*/*z* 493, 511, and 529 as $(UO_2)(H_3L)(H_2O)_x{}^+$, where $x = 1-3$, and at *m*/*z* 574−577, 593−595, and 629−631 as cluster complexes with H_2O and $HClO_4$. Also, a number of MH_jL_2 species containing different numbers of protons as well as H_2O and $HClO_4$ are observed in the region from *m*/*z* 681 to 1050. A peak at *m*/*z* 1155 is assigned to a 2:3 cluster complex, $(UO_2)_2(H_3L)(H_2L)(H_4L)^+$. This complex is not expected to form in the feed solution according to the results by potentiometry. It probably formed during the ESI-MS process including steps of droplet formation, droplet shrinkage, and gaseous ion formation.

In the negative mode, fewer species were observed. Besides the 1:1 complexes at *m*/*z* 509−511 and 545−547 and the 1:2 complexes at *m*/*z* 679 and 701, the "free" uranyl ion (not complexed with HEDPA) was observed at *m*/*z* 567−569 as clusters with $HClO_4$. These data support the results from potentiometry that indicate that U^{VI} predominantly forms 1:1 and 1:2 complexes with HEDPA under the experimental conditions. In fact, speciation calculation with the stability constants in Table 2 shows that this solution contains 30% free $UO_2{}^{2+}$, 35% $UO_2H_3L^+$, and 35% $UO_2H_4L_2{}^{2-}$. It is interesting to notice that a dimeric complex, $(UO_2)_2(H_2L)_2Cl^-$, was also observed, though the speciation calculation predicts that the dimeric complexes are negligible in this solution.

As the pH of the solutions was increased, the signal-to-noise ratio of the ESI-MS data deteriorated, making it difficult to identify the peaks with high certainty. No useful data were obtained for solutions with pH higher than 7. For solutions of pH from 4 to 7, 1:2 complexes were still dominant, but the 2:2 dimeric complexes $(UO_2)_2(H_jL)_2$ gradually become significant. Again, these data confirm the stoichiometric ratio of M:L predicted by the thermodynamic measurement with potentiometry.

The U^{VI}HEDPA cluster complexes containing H_2O and $HClO_4$ observed in this study are in good agreement with the observations by Jacopin et al.[10] From the data of an ESI-MS titration, Jacopin et al. were able to identify the UO_2H_jL and $UO_2H_jL_2$ species and calculate the "conditional" stability constant of $UO_2H_3L^+$.[10] However, taking the possible experimental artifacts of the ESI-MS experiments into consideration, we intend to use our ESI-MS data on a qualitative basis, only to confirm the stoichiometric ratio of M:L predicted by thermodynamic measurements.

3.4.2. NMR. The ^1H-decoupled ^{31}P NMR spectra of HEDPA in the absence of U^{VI} are shown in Figure 5a. A single peak around 21 ppm was observed for solutions at different pHs, indicating that the two phosphorus nuclei in HEDPA are identical and that the ligand species, $H_jL^{-(4-j)}$ where $j = 0-4$, exchange fast in solution so that only the average chemical shift was observed on the time scale of NMR. As the pH was increased from 1.3 to 12.6, the chemical shift changed from 21.5 to 20.7 ppm, reflecting the effect of deprotonation on the speciation. The small change (<1 ppm) suggests that the dissociation of protons on the phosphonic acid groups has a small effect on the shielding of the phosphorus nuclei.

The ^1H-decoupled ^{31}P NMR spectra of HEDPA in the presence of U^{VI} are shown in Figure 5b. Three major peaks around 21 ppm (A), 24 ppm (B), and 27 ppm (C) were observed. On the basis of the NMR spectra of HEDPA in

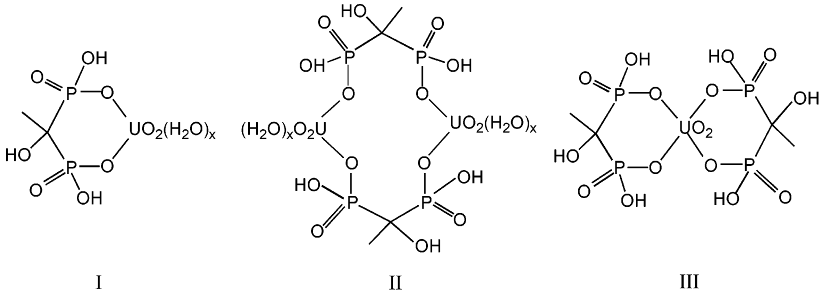

Figure 6. Proposed structures of U^{VI}HEDPA complexes: (I) a 1:1 complex, UO_2H_2L;[10] (II) a 2:2 complex, $(UO_2)_2(H_2L)_2$; (III) a 1:2 complex, $UO_2(H_2L)_2$.[10]

Figure 5a, peak A can be assigned to the uncomplexed ligand species. The position of peak B, downfield from peak A by 3 ppm, agrees with that previously observed and assigned by Jacopin et al. to the 1:2 ($UO_2H_4L_2$) complex.[10] Taking into consideration the complexes identified by potentiometry (Table 2) and ESI-MS (Table S1 in the Supporting Information) and the fact that peak B slightly shifted upfield as the pH was increased, we have assigned peak B to the average effect of a number of 1:2 complexes ($UO_2H_jL_2$) that span from $UO_2H_4L_2$ at low pH to UO_2L_2 at high pH. Exchange between these species occurs by protonation and deprotonation and is likely to be fast so that only a single peak was observed. The position of peak C, downfield from peak A by 6 ppm, appears to agree with that previously assigned to the 1:1 (UO_2H_2L) complex.[10] However, we cannot assign peak C to the 1:1 complexes because they are negligible under the present conditions. Instead, peak C can be assigned to the 2:2 complexes, $(UO_2)_2H_jL_2$, that could form in near-neutral and slightly basic solutions. In fact, a few such species were observed by ESI-MS in solutions with pH from 2 to 7. Again, peak C reflects the average effect of the 2:2 complexes containing different numbers of protons, $(UO_2)_2HL_2$ and $(UO_2)_2L_2$. The gradual upfield shift of peak C with the increase of pH supports this assignment.

We have made efforts to obtain structural information on the U^{VI}HEDPA complexes by X-ray crystallography and extended X-ray absorption fine structure (EXAFS). However, attempts to prepare single crystals of the U^{VI}HEDPA complexes were unsuccessful. Data from EXAFS experiments were not sufficiently informative to reveal the structures of complexes in solution. At present, we can only discuss the NMR data based on the proposed structures shown in Figure 6. Complexation of the phosphonic acid group(s) with UO_2^{2+} reduces the shielding on the phosphorus nuclei so that the ^{31}P NMR chemical shifts for the complexes would shift downfield relative to that of the uncomplexed ligand, which is consistent with the downfield position of peaks B (1:2 complexes) and C (2:2 complexes) relative to that of peak A (uncomplexed ligand). Furthermore, the effect of complexation on the shielding would be larger in the 1:1 (I) and 2:2 (II) complexes than in the 1:2 complex (III) because the electrical charge of UO_2^{2+} is shared by two phosphonic acid groups in the former (I and II) but by four phosphonic acid groups in the latter (III). Therefore, it is reasonable to assign peak C (27 ppm) to the 2:2 (or 1:1) complexes and peak B (24 ppm) to the 1:2 complexes.

4. Summary

This work extends the study of the complexation between U^{VI} and HEDPA from strongly acidic solutions to neutral and basic solutions. Thermodynamic parameters of complexation were determined by potentiometry and calorimetry. Spectroscopic techniques (UV−vis absorption spectrophotometry, ESI-MS, and NMR) provided support for the stoichiometry of complexes in solution. It was observed that U^{VI} forms a number of 1:1, 1:2, and 2:2 complexes with HEDPA in solution. The complexes range from highly protonated (e.g., UO_2H_3L and $UO_2H_4L_2$) in strongly acidic solutions to unprotonated (e.g., UO_2L_2) and mixed hydroxyl−HEDPA complexes (e.g., $UO_2(OH)L_2$) in neutral and basic solutions. The thermodynamic data from this study are of importance in the interpretation and prediction of the chemical behavior of U^{VI} in the alkaline leaching of nuclear waste sludges.

Acknowledgment. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences and Office of Biological and Environmental Research under U.S. Department of Energy Contract DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory (LBNL). The authors thank Dr. W. Lukens of LBNL for technical help with the NMR experiments and Dr. H. van Halbeek and Dr. U. Andersen of the NMR and Mass Spectrometry Facilities of the College of Chemistry, University of California, Berkeley, Berkeley, CA, for technical assistance with the NMR and ESI-MS experiments.

Supporting Information Available: Observed peaks (*m*/*z*) in ESI-MS experiments and the assignments (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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