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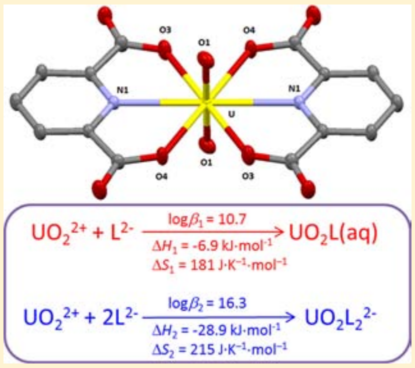
Complexation of U(VI) with Dipicolinic Acid: Thermodynamics and Coordination Modes

Chao Xu,[†,‡] Guoxin Tian,[†] Simon J. Teat,[§] and Linfeng Rao*[,†]

[†]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
[‡]Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, People's Republic of China
[§]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Ⓢ *Supporting Information*

ABSTRACT: Complexation of UO_2^{2+} with dipicolinic acid (DPA) has been investigated in 0.1 M $NaClO_4$. The stability constants (log β_1 and log β_2) for two successive complexes, UO_2L and $UO_2L_2^{2-}$ where L^{2-} stands for the deprotonated dipicolinate anion, were determined to be 10.7 ± 0.1 and 16.3 ± 0.1 by spectrophotometry. The enthalpies of complexation (ΔH_1 and ΔH_2) were measured to be $-(6.9 \pm 0.2)$ and $-(28.9 \pm 0.5)$ $kJ{\cdot}mol^{-1}$ by microcalorimetry. The entropies of complexation (ΔS_1 and ΔS_2) were calculated accordingly to be (181 ± 3) and (215 ± 4) $J{\cdot}K^{-1}{\cdot}mol^{-1}$. The strong complexation of UO_2^{2+} with DPA is driven by positive entropies as well as exothermic enthalpies. The crystal structure of $Na_2UO_2L_2(H_2O)_8(s)$ shows that, in the 1:2 UO_2^{2+}/DPA complex, the U atom sits at a center of inversion and the two DPA ligands symmetrically coordinate to UO_2^{2+} via its equatorial plane in a tridentate mode. The structural information suggests that, due to the conjugated planar structure of DPA with the donor atoms (the pyridine nitrogen and two carboxylate oxygen atoms) arranged at optimal positions to coordinate with UO_2^{2+}, little energy is required for the preorganization of the ligand, resulting in strong UO_2^{2+}/DPA complexation.



■ INTRODUCTION

The advanced nuclear energy system calls for more efficient and environmentally sustainable separation processes for spent nuclear fuel (SNF) reprocessing. It is critically important to precisely control the chemical behavior of actinides and fission products and minimize the amount of hazardous nuclear wastes. Recently, amide derivatives of dicarboxylic acids have been actively studied as extractants for actinide separations because of their potential to make the separation processes more efficient and environmentally benign.[1−7] The amide ligands contain only C, H, O, and N atoms so that they are completely incinerable (so-called "CHON" principle). As a result, the amount of solid radioactive wastes generated in the amide-based processes could be significantly reduced when compared to traditional processes using organophosphorus or sulfur-containing extractants. Among the ligands, the amide/diamide derivatives of dipicolinic acid (DPA) have been shown to be effective for extracting actinides in various oxidation states.[5−10] DPA itself is also a widely employed complexing agent known to strongly bind various metals in versatile modes.[11−15]

To help with the development of "CHON" ligands for efficient separations in the advanced nuclear energy system, it is necessary to understand the thermodynamic principles and structural factors that govern the complexation of DPA with actinide ions. In previous work,[16] we have studied the complexation of DPA with Np(V), a problematic element in SNF reprocessing, and determined thermodynamic parameters and coordination modes in Np(V)/DPA complexes. As to uranium, the most abundant actinide element in SNF reprocessing, although the structures of a number of solid U(VI)/DPA compounds[17−23] and the kinetics of U(VI)/DPA complexation[24] have been reported, thermodynamic data on U(VI)/DPA complexation are nearly nonexistent. There have been no values of enthalpy and entropy of complexation, and only a single study where the stability constant of the 1:1 U(VI)/DPA complex was determined to be $10^{5.70}$ by pH titrations.[25] We believe that this value is erroneous and much too low in comparison with the 1:1 DPA complexes with other cations. For example, the stability constant of the 1:1 DPA complex with NpO_2^+, an actinyl cation with much lower effective charge than UO_2^{2+} (+2.2 for NpO_2^+ vs +3.2 for UO_2^{2+}),[26] was $10^{8.7}$,[16] 3 orders of magnitude higher than the literature value of $10^{5.70}$ for the 1:1 U(VI)/DPA complex. The lack of thermodynamic data and the error in the single data available are probably due to the fact that the high strength of U(VI)/DPA complexes necessitates the use of competition methods that are more elaborate and less familiar. In this work, we adopted a method of two-step competition spectrophotometry, including the determination of the strong stability constant of the 1:1 U(VI)/DPA complex using Sc^{3+} as a competing cation, and the subsequent determination of the stability constant of the 1:2 U(VI)/DPA complex using H^+ as

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the competing cation. The enthalpies of complexation were determined by microcalorimetry. The crystal structure of a sodium salt of the 1:2 U(VI)/DPA complex was also obtained. Integration of the thermodynamic and structural data allows comparison between DPA and related aminodicarboxylic acids (Figure 1), provides insight into the driving force of the complexation between U(VI) and DPA, and helps to develop ligands containing nitrogen donors for separations of actinides in advanced nuclear systems.

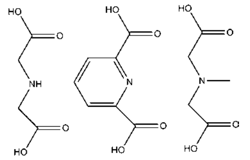

Figure 1. (From left to right) iminodiacetic acid (IDA), dipicolinic acid (DPA), *N*-methyl-iminodiacetic acid (MIDA).

EXPERIMENTAL SECTION

Chemicals. All chemicals were reagent grade or higher. Milli-Q water was used in preparation of all the solutions. All experiments were conducted at (23 ± 1)°C (or otherwise stated) and an ionic strength of 0.1 M ($NaClO_4$). The stock solution of U(VI) in perchloric acid was prepared as described elsewhere.[27] The concentration of U(VI) in the stock solution was determined by absorption spectrophotometry and fluorimetry.[28] The stock solution of Sc(III) was prepared by dissolving Sc_2O_3 in concentrated perchloric acid under stirring and heating, and then diluting to desired concentrations with H_2O. The concentration of Sc(III) was determined by complexometric titrations with ethylenediaminetetraacetic acid (EDTA) using xylenol orange as the indicator. The concentrations of perchloric acid in the stock solutions of U(VI) and Sc(III) were determined by Gran's titration.[29] Dipicolinic acid (or pyridine-2,6-dicarboxylic acid, DPA, 98%) from Avocado Research Chemicals Ltd. was used as received. Buffered DPA solutions were prepared by neutralizing weighted amounts of DPA with a standard NaOH solution (0.1002 M, Brinkmann) and diluting to appropriate concentrations.

In this work, $H_2L(aq)$, HL^-, and L^{2-} denote the protonated and deprotonated species of the DPA ligand.

Spectrophotometry. Competition spectrophotometric titrations were carried out on a Cary 6000i spectrophotometer (Varian Inc.) to determine the stability constants of UO_2^{2+}/DPA complexes with Sc^{3+} (for the 1:1 UO_2^{2+}/DPA complexation) or H^+ (for the stepwise 1:2 UO_2^{2+}/DPA complexation) as the competing cations. Absorption spectra were collected in the wavelength region of 210−340 nm (0.2 nm interval), where the species of DPA and its complexes with UO_2^{2+} and Sc^{3+} had characteristic absorption spectra. For a typical titration, 2.00 mL of the UO_2^{2+}/DPA solution was placed in a quartz cuvette with 1.0 cm optical path, into which appropriate aliquots of Sc^{3+} or $HClO_4$ solutions were added and mixed thoroughly (for 1−2 min) before the spectra were collected. Preliminary kinetic experiments showed that the complexation reaction was fast and the absorbance became stable within 30 s of mixing. Usually, 15−20 additions were made, generating a set of 16−21 spectra in each titration. Multiple titrations with different concentrations of DPA or U(VI) were performed. The stability constants of UO_2^{2+}/DPA complexes were calculated by the nonlinear regression program Hyperquad 2008.[30] In the calculation, auxiliary data were used, including the protonation constants of DPA that were taken from the literature[31] and confirmed by this work and the stability constants of the Sc(III)/DPA complexes that were determined in this work. The confirmation and determination of the auxiliary data are described in the Supporting Information, SI.

Microcalorimetry. Calorimetric titrations were conducted at 25 °C with an isothermal microcalorimeter (Model ITC 4200, Calorimetry Sciences Corp.). Procedures and results of the calibration of the calorimeter were provided elsewhere.[32] In all titrations, 0.9 mL of U(VI) solution was placed in the reaction cell and titrated with a DPA solution. A total of *n* additions of 0.005 mL DPA solution were made (n = 45−50) through a 0.250 mL syringe, resulting in *n* experimental values of total heat ($Q_{ex,j}$, $j = 1 - n$). These values were corrected by the heats of titrant dilution ($Q_{dil,j}$) that were measured in a separate run. The net reaction heat at the *j*th point ($Q_{r,j}$) was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. The value of $Q_{r,j}$ is a function of the concentrations of the reactants (C_U, C_H, and C_{DPA}), the equilibrium constants and the enthalpies of the reactions that occurred in the titration. The computer program HyperDeltaH[33] was used to calculate the enthalpies of complexation of UO_2^{2+} with DPA. In the calculation, the protonation constants and enthalpies of DPA from the literature[31] were used.

Single Crystal X-ray Diffractometry. Pale yellow crystals of the sodium salt of the 1:2 U(VI)/DPA complex, $Na_2UO_2(DPA)_2(H_2O)_8$, were obtained by slow evaporation of a solution containing $UO_2(ClO_4)_2$ and DPA (a molar ratio of 2 for U/DPA) at neutral pH. Representative crystals were selected and attached on the end of a MiTeGen loop with paratone oil and mounted on the goniometer. Diffraction data were collected on a Bruker APEX II diffractometer at Beamline 11.3.1 of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. Details of the crystallographic data are provided in Table 1.

RESULTS

Stability Constants of the U(VI)/DPA Complexes. *The 1:1 U(VI)/DPA Complex.* On the basis of the structural features of DPA and the structural and thermodynamic data in the literature on the complexation of DPA with Np(V)[16] and other cations,[31] it was reasonable to assume that DPA could form two successive complexes with U(VI) in aqueous solutions. Preliminary potentiometric titration experiments suggested that the 1:1 U(VI)/DPA complexation was too strong to be quantified directly by potentiometry or spectrophotometry without introducing proper competing ligands or metal ions. After taking into consideration various potential competing cations, Sc^{3+} was selected in this work as a competing agent for the complexation of DPA because it has no UV absorption and it may form DPA complexes with strength comparable to those of U(VI)/DPA complexes. In this case, the stability constants of the Sc^{3+}/DPA complexes must be known and accurate. One set of stability constants for the Sc^{3+}/DPA complexes were available in the literature, but were obtained in a different ionic medium ($\log \beta_1 = 11.2$ and $\log \beta_2 = 18.9$ at $I = 0.5$ M $NaClO_4$).[34] Therefore, auxiliary potentiometric and spectrophotometric experiments were first conducted to determine the stability constants of the Sc^{3+}/DPA complexes in 0.1 M $NaClO_4$, as described in the SI. The values obtained ($\log \beta_1 = 11.7 \pm 0.1$ and $\log \beta_2 = 19.8 \pm 0.1$) were in good accordance with the literature data[34] given the difference in the ionic strength.

The optical absorption of DPA in the UV region was used to probe the complexation in the spectrophotometric titration experiments. Figure 2 shows a representative titration of a U(VI)/DPA solution with a Sc(III) solution. As the Sc(III) solution was added, the absorption bands around 270 and 280 nm were intensified and slightly blue-shifted, while the absorbance below 265 nm significantly decreased. The variations of the spectra clearly showed the competition of Sc^{3+} with UO_2^{2+} for complexing DPA. With the stability constants of the Sc^{3+}/DPA complexes determined in this work (see the SI), the best fit was achieved by assuming that the 1:1 UO_2^{2+}/DPA complex, $UO_2L(aq)$ where L^{2-} denotes the

Table 1. Crystal Data and Structure Refinement for $Na_2UO_2(DPA)_2(H_2O)_8$

chemical formula	$C_{14}H_{22}N_2Na_2O_{18}U$
formula weight	790.35
temperature	296(2) K
radiation, wavelength	synchrotron, 0.77490 Å
crystal system, space group	monoclinic, $C2/m$
unit cell parameters	a = 15.397(8) Å α = 90° b = 7.036(4) Å β = 124.316(5)° c = 13.178(11) Å γ = 90°
cell volume	1179.1(13) $Å^3$
Z	2
calculated density	2.226 g/cm^3
absorption coefficient μ	3.845 mm^{-1}
$F(000)$	756
crystal color and size	pale yellow, 0.03 × 0.03 × 0.01 mm^3
reflections for cell refinement	4333 (θ range 4.05 to 31.95°)
data collection method	Bruker APEX II CCD diffractometer ω rotation with narrow frames
θ range for data collection	4.08 to 33.87°
index ranges	h −22 to 22, k −10 to 10, l −18 to 18
completeness to θ = 30.00°	99.5%
reflections collected	8659
independent reflections	1962 (R_{int} = 0.0350)
reflections with $F^2 > 2\sigma$	1953
absorption correction	semiempirical from equivalents
min. and max. transmission	0.83 and 0.93
structure solution	direct methods
refinement method	full-matrix least-squares on F^2
weighting parameters a, b	0.0674, 0.0000
data/restraints/parameters	1962/12/113
final R indices [$F^2 > 2\sigma$]	$R1$ = 0.0336, $wR2$ = 0.0891
R indices (all data)	$R1$ = 0.0338, $wR2$ = 0.0893
goodness-of-fit on F^2	1.059
largest and mean shift/su	0.000 and 0.000
largest diff. peak and hole	2.216 and −1.489 e $Å^{-3}$

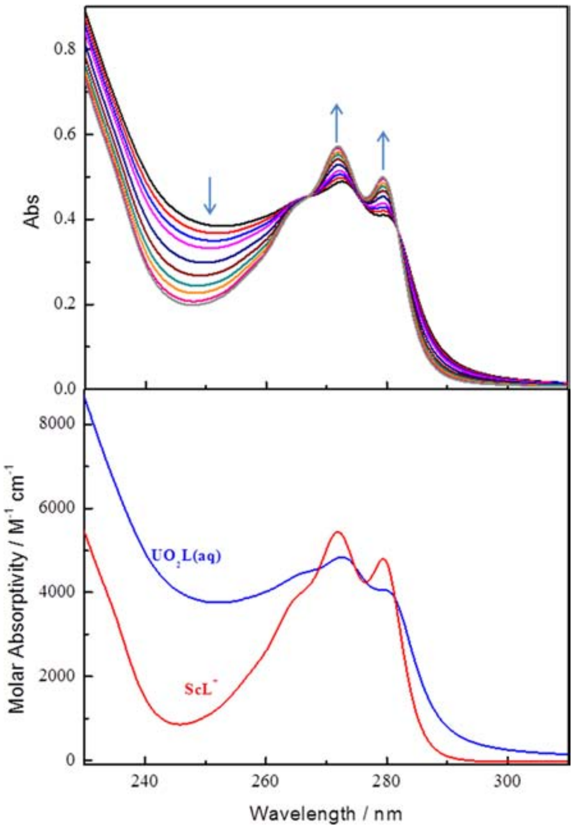

Figure 2. Spectrophotometric titrations of U(VI)/DPA with Sc(III). Initial solution: V^0 = 2.00 mL, $C_H{}^0/C_{DPA}{}^0/C_U{}^0$ = 2.2/0.10/0.12 mmol·dm^{-3}; Titrant: 1.0 mmol·dm^{-3} Sc^{3+}/4.8 mmol·dm^{-3} H^+, 0.38 mL added. (Upper) absorption spectra normalized in terms of $C_{DPA}{}^0$. (Lower) calculated molar absorptivities of $UO_2L(aq)$ (blue) and ScL^+ (red).

dipicolinate anion, was dominant in the beginning of the titration but gradually decreased due to the formation of the 1:1 Sc^{3+}/DPA complex. The stability constant ($\log\beta_1$) of UO_2L(aq) was accordingly calculated to be 10.7 ± 0.1. Under the experimental conditions, the 1:2 Sc^{3+}/DPA and $UO_2{}^{2+}$/DPA complexes were insignificant. Figure 2 also shows the calculated molar absorptivities of ScL^+ and UO_2L(aq). The molar absorption spectra of ScL^+ calculated from the $Sc^{3+}/UO_2{}^{2+}$ competition titrations (Figure 2) were identical to those of ScL^+ obtained in the auxiliary spectrophotometric experiments (see the SI).

The 1:2 U(VI)/DPA Complex. Preliminary experiments indicated that the second stepwise complexation of $UO_2{}^{2+}$ with DPA was much weaker than the first so that the stepwise stability constant of $UO_2L_2{}^{2-}$ could be determined in acidic DPA solutions by utilizing the competition between protons and $UO_2{}^{2+}$. Figure 3 shows the variations of the absorption spectra when the U(VI)/DPA solution was titrated with $HClO_4$. The variations could be attributed to the changes in the distribution of various species of DPA including HL^-, H_2L(aq), UO_2L(aq), and $UO_2L_2{}^{2-}$. Among these species, the individual molar absorption spectra of the first three were already known—those of HL^- and H_2L(aq) were obtained by auxiliary spectrophotometric titrations (see the SI), whereas that of UO_2L(aq) was determined by the titrations described above (Figure 2). Aided by the known molar absorption spectra of the three species, we were able to fit the spectra shown in Figure 3 (upper figure) and obtain the stability constant and molar absorptivity of $UO_2L_2{}^{2-}$. The $\log\beta_2$ of $UO_2L_2{}^{2-}$ was found to be 16.3 ± 0.1 (stepwise log K_2 = 5.6). It is worth noting that the similarities in the molar absorption spectra of UO_2L(aq) and $UO_2L_2{}^{2-}$ (Figure 3, lower figure) imply that the coordination modes of the DPA ligands in the two complexes are very similar. Such similarities also suggest it would be extremely difficult, if not impossible, to simultaneously determine the stability constants of both UO_2L(aq) and $UO_2L_2{}^{2-}$ by spectrophotometric titrations. Such difficulty necessitates the use of a two-step method, such as the one used in this work, including the determination of the stability constant of UO_2L(aq) by competition titration with Sc^{3+} and the subsequent determination of the stability constant of $UO_2L_2{}^{2-}$.

Enthalpy of Complexation. Figure 4 shows two representative calorimetric titrations of U(VI)/DPA complexation, in which the DPA ligand was added into the U(VI)

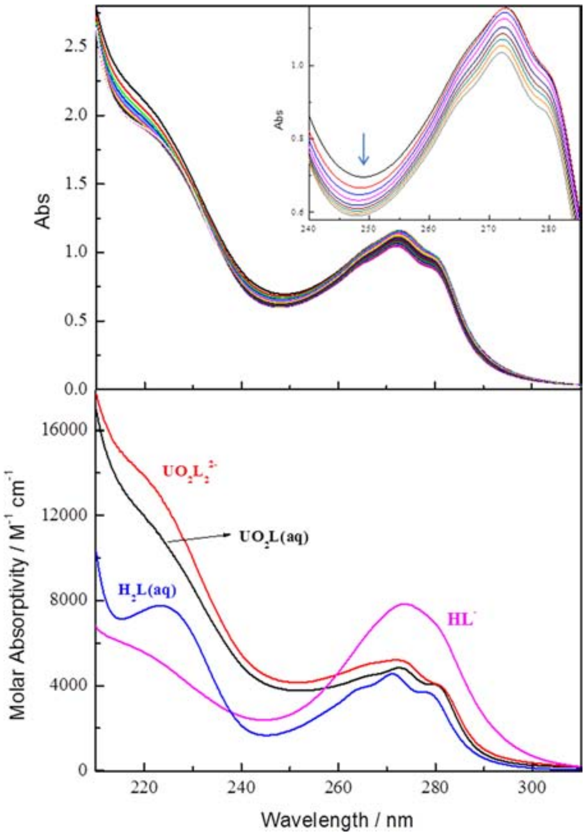

Figure 3. Spectrophotometric titrations of U(VI)/DPA with $HClO_4$. Initial solution: V^0 = 2.00 mL, $C_H{}^0/C_{DPA}{}^0/C_U{}^0$ = 1.1/0.20/0.10 mmol·dm^{-3}; Titrant: 0.10 mol·dm^{-3} $HClO_4$, 0.36 mL added. (upper) 18 spectra normalized in terms of $C_{DPA}{}^0$ with the inset showing 9 enlarged spectra from 240 to 285 nm. (lower) Molar absorptivities of HL^- (purple red), $H_2L(aq)$ (blue), $UO_2L(aq)$ (black), and $UO_2L_2{}^{2-}$ (red, the magnitude of absorptivity was scaled down to 1/2).

solutions. The patterns of the thermogram (upper figures) clearly indicated that the 1:1 U(VI)/DPA complex was very strong so that each addition of DPA was completely complexed with U(VI) (the plateau portion of the thermogram with constant heat rates), while the second stepwise complexation (1:2 complex) was moderate (the second portion of the thermogram with decreasing heat rates). These observations were consistent with the stability constants determined by spectrophotometry (log β_1 = 10.7 and log K_2 = 5.6, stepwise).

Since the solubility of the 1:2 U(VI)/DPA complex was found to be low, titration conditions were carefully selected so that precipitation was avoided. The total reaction heat, $Q_{r,i}$, as well as the distribution of U(VI) species, is shown as a function of the titrant volume in Figure 4 (lower figure). From the reaction heat and the stability constants of $UO_2L(aq)$ and $UO_2L_2{}^{2-}$ obtained by spectrophotometry, the enthalpies of complexation of $UO_2L(aq)$ and $UO_2L_2{}^{2-}$ were calculated to be −(6.9 ± 0.2) and −(28.9 ± 0.5) kJ·mol^{-1}, respectively. From the stability constants and the enthalpies, the entropies of complexation for $UO_2L(aq)$ and $UO_2L_2{}^{2-}$ were accordingly calculated to be (181 ± 3) and (215 ± 4) J·K^{-1}·mol^{-1}, respectively. The thermodynamic parameters are summarized in Table 2.

Crystal Structure of $Na_2UO_2L_2(H_2O)_8$. The sodium salt of the 1:2 U(VI)/DPA complex, $Na_2UO_2L_2(H_2O)_8$, crystallized in a monoclinic space group, *C*2/*m*. The structure is shown in Figure 5. Selected bond lengths (Å) and bond angles (deg) are provided in Table 3.

In the unit cell, the U atom is located at an inversion center. The axial O=U=O moiety is perfectly linear (180° angle) and symmetrical (the two U=O bonds are equal in length, 1.753(6) Å). The O=U=O moiety is coordinated equatorially by two DPA ligands. Each ligand is tridentate and coordinates to U with the N atom of the pyridine and two O atoms of two different carboxylate groups. The bond lengths between U and the two carboxylate oxygens are slightly different (R_{U-O3} = 2.437(5) Å and R_{U-O4} = 2.479(7) Å) and one oxygen (O4) is slightly aberrant away from the coplane of the two DPA ligands.

■ DISCUSSION

Thermodynamic Trends in U(VI) Complexation with Structurally Related Ligands. *In Comparison with Simple Dicarboxylic Acids.* Data in Table 2 show that DPA forms 1:1 U(VI) complexes that are 5−6 orders of magnitude stronger than malonate or phthalate. Similarly, the U(VI) complexes with two iminodiacetic acids (IDA and MIDA) are also significantly stronger than the U(VI)/malonate or U(VI)/phthalate complexes. Obviously, DPA and the iminodiacetic acids gain stronger binding strength due to the participation of the nitrogen in the coordination. Such increases in binding strength are manifested mainly by the difference in the enthalpy of complexation between the N-donor ligands and simple carboxylic ligands discussed in more detail below.

The enthalpies of 1:1 U(VI) complexation with DPA, IDA, and MIDA are −6.9, −2, and +4 kJ·mol^{-1}, respectively, all being more favorable to the complexation than that of malonate (+8 kJ·mol^{-1}). Using the concept of "residual" enthalpy from Choppin's earlier work[36] and correcting the enthalpy contribution from the two carboxylate groups, the enthalpy contributions from the nitrogen coordination are −14.9, −10, and −4 kJ·mol^{-1} for the U(VI) complexes of DPA, IDA, and MIDA, respectively. The exothermic enthalpy of N-coordination with U(VI) suggests that the nitrogen donor in these ligands is much less hydrated than the oxygen of the carboxylate group and needs much less energy to dehydrate, resulting in more favorable enthalpy of complexation.

In Comparison among the N-Donor Ligands (DPA, MIDA, IDA). The strength of 1:1 U(VI) complexes follows the order: DPA > MIDA (*N*-methyliminodiacetic acid) > IDA (iminodiacetic acid) (see the structure schematics in Figure 1). The observation that MIDA forms a stronger U(VI) complex than IDA could be rationalized by the difference in the basicity of the two ligands—the pK_a of HL is 9.59 for MIDA and 9.34 for IDA at 25 °C and 0.1 M ionic strength.[31] The electron-donating methyl group makes the nitrogen as well as the carboxylate group of MIDA more basic than those of IDA, resulting in stronger complexation of U(VI) with the former. However, the same rationalization cannot explain why DPA forms much stronger complex with U(VI) than IDA or MIDA, since the pK_a of DPA is only 4.7 under similar conditions.[31] We believe that the strong binding ability of DPA probably results from its "rigid" and conjugated planar structure in which the pyridine nitrogen and two carboxylate oxygen atoms are arranged at optimal positions to coordinate with $UO_2{}^{2+}$ through its equatorial plane. As shown in Table 3, the ∠O−U−N angles are all very close to 60 degrees and the six donor atoms (4 O and 2 N) coordinate with U forming four 5-membered rings in a nearly perfect hexagonal structure. The rigid planar structure of DPA helps to reduce the preorganization energy that is

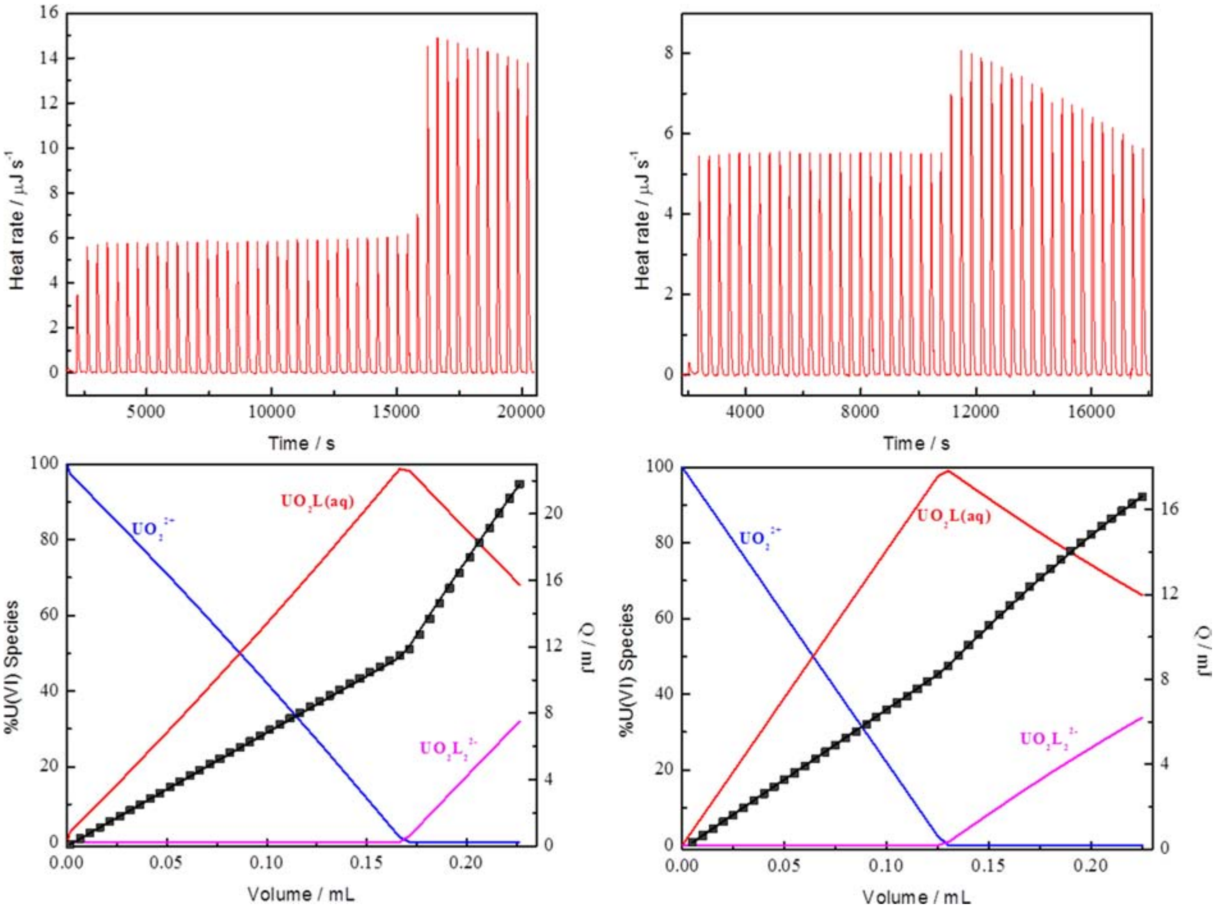

Figure 4. Microcalorimetric titrations of U(VI)/DPA complexation (t = 25 °C, I = 0.1 mol·dm^{-3} $NaClO_4$). Titrant: 9.8 mmol·dm^{-3} Na_2DPA (about 45 additions of 0.005 mL each). Initial cell solution: (left) V^0 = 0.900 mL, $C_H{}^0$ = 2.1 mmol·dm^{-3}, $C_U{}^0$ = 2.2 mmol·dm^{-3}; (right) V^0 = 0.900 mL, $C_H{}^0$ = 7.0 mmol·dm^{-3}, $C_U{}^0$ = 1.55 mmol·dm^{-3}. (Top) thermogram; (bottom) total heat (right y axis; closed symbol, experimental; line, calculated) and speciation of U(VI) (left y axis; lines, blue, UO_2^{2+}; red, $UO_2L(aq)$; purple, $UO_2L_2^{2-}$) versus the volume of the titrant.

Table 2. Thermodynamic Parameters of the Complexation of UO_2^{2+} with DPA (t = (23 ± 1) °C, I = 0.1 mol·dm^{-3} $NaClO_4$)[a]

reaction	ligand	log β	ΔH kJ·mol^{-1}	ΔS J·K^{-1}·mol^{-1}	ref
$UO_2^{2+} + L^{2-} = UO_2L(aq)$	DPA	10.7 ± 0.1	−6.9 ± 0.2[b]	181 ± 3	p.w.
		5.70[c]			25
	IDA	8.96	−2	160	31
	MIDA	9.71	+4	200	31
	MA	5.36	+8.0	130	35
	PA	4.81			31
$UO_2^{2+} + 2L^{2-} = UO_2L_2^{2-}$	DPA	16.3 ± 0.1	−28.9 ± 0.5	215 ± 4	p.w.
	PA	7.73			31

[a] Data for other ligands from the literature are for comparison (IDA: iminodiacetic acid; MIDA: *N*-methyl-iminodiacetic acid; MA: malonic acid; PA, phthalic acid). Legends: p.w., present work. [b] t = 25 °C. [c] I = 0.1 mol·dm^{-3} KNO_3.

otherwise required in the complexation of U(VI) with more flexible ligands such as IDA or MIDA. The same order of binding strength (DPA > MIDA > IDA) was also observed for the complexation of NpO_2^+ and discussed in terms of the difference in the preorganization energy and the basicity on the nitrogen.[16]

In fact, comparison of the structural information between the U(VI) complexes with IDA[37] and lanthanide complexes with IDA[36] and DPA[36,38] and the U(VI)/DPA complex from this work provides support for the above argument that the "rigid" and conjugated planar structure of DPA facilitates the coordination of the nitrogen and strengthens the complexation. Using ^{15}N NMR and EXAFS, Jiang et al. observed the coordination of the nitrogen in IDA to UO_2^{2+}, with a U−N distance of 2.92 Å,[37] much longer than the U−N distance of 2.64 Å in the U(VI)/DPA complex (Table 3). Such difference could be explained by the fact that IDA does not have a rigid and conjugated planar structure as DPA. The nitrogen of IDA coordinates to UO_2^{2+} with a lone electron pair in a configuration of sp^3 hybridization, while the nitrogen of DPA coordinates to UO_2^{2+} with a lone electron pair in a configuration of sp^2 hybridization that perfectly fits into the equatorial plane of UO_2^{2+}. Besides, the imino N−H bond in IDA is conformationally flexible and can flip above or below the equatorial plane of UO_2^{2+}, resulting in a more labile U−N coordination bond. In fact, several lines of evidence in

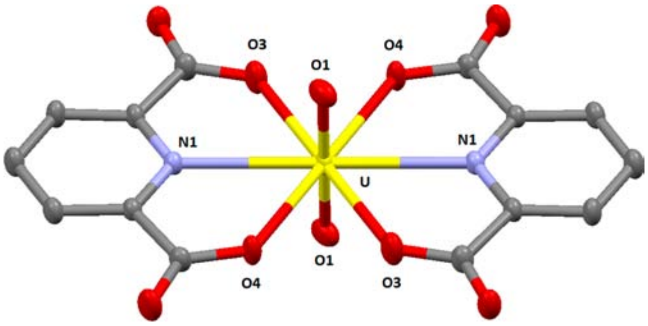

Figure 5. Crystal structure of the sodium salt of the 1:2 U(VI)/DPA complex, $Na_2UO_2L_2(H_2O)_8$ (25% probability ellipsoids). The H and Na atoms and water molecules are not shown for clarity. U, yellow; O, red; C, gray; and N, blue.

lanthanide complexation, including data from PMR (paramagnetic NMR) studies[38] with ^{139}La, showed that the ligand exchange rate of the Ln/DPA complex is much slower than that of the Ln/IDA complex, and suggested that the distance of Ln−N in the former is shorter than that in the latter. The structural data, including U(VI)/DPA from this work, U(VI)/IDA,[37] lanthanide/IDA and lanthanide/DPA,[38] all suggest that the rigid and conjugated planar structure of DPA facilitates the nitrogen coordination and enhances the complexation with U(VI).

Implication for the Complexation of U(VI) with Dipicolinamides. Previous studies have shown that oxidicarboxylic acid (ODA) and its diamide derivative (tetramethyl-3-oxa-glutaramide, TMOGA) form tridentate U(VI) complexes with similar structures, but the contributions of enthalpy and entropy to the stability of the complexes differ between the acid complex and the amide complex.[27] By analogy, the results on the complexation of U(VI) with DPA from this work have the following implications: (1) Dipicolinamides are expected to form tridentate complexes with U(VI) with similar structures as in the U(VI)/DPA complexes. (2) The enthalpy of U(VI)/dipicolinamide complexation would be more exothermic and more favorable than that of U(VI)/DPA complexation, because the −C=O unit in the amide group has been shown to be less solvated and requires less desolvation energy than the $-COO^-$ unit in the carboxylate group.[27] More favorable enthalpy could make dipicolinamides stronger complexants than DPA and potentially excellent extractants for U(VI). (3) In contrast to the effect of enthalpy, the entropy of U(VI)/dipicolinamide complexation would be smaller and less favorable than that of U(VI)/DPA complexation, because fewer solvent molecules are released in the complexation with amides than carboxylates.[27] This means that, to strengthen the complexation of dipicolinamides with U(VI) and improve its efficiency in extracting U(VI), enlarging the entropy effect (e.g., designing picolinamides of higher denticity) should be a plausible approach.

■ CONCLUSIONS

Thermodynamic parameters including stability constants, enthalpies, and entropies for U(VI)/DPA complexes were determined systematically by absorption spectroscopy and calorimetry for the first time. DPA was found to form strong complexes with U(VI) with favorable enthalpies and entropies. The higher binding strength of DPA, in comparison with that of simple dicarboxylic acids and iminodiacetic acids, arises from the participation of the nitrogen and its rigid conjugated planar structure that requires less preorganization energy for coordination. Data from this work provide help with the development of dipicolinamide ligands that have the potential to be used as efficient extractants for actinide separations in advanced nuclear energy systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Potentiometric and spectrophotometric data for determining the stability constants of Sc(III)/DPA complexes, and one file for structural information (U-DPA.cif). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: 510 486 5427. Fax: 510 486 5596. E-mail: LRao@lbl.gov.

Notes

The authors declare no competing financial interest.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) in $Na_2UO_2L_2(H_2O)_8$

U(1)−O(1)	1.753(6)	U(1)−O(1A)	1.753(6)
U(1)−O(3)	2.437(7)	U(1)−O(3A)	2.437(7)
U(1)−N(1)	2.641(5)	U(1)−N(1A)	2.641(5)
U(1)−O(4)	2.479(5)	U(1)−O(4A)	2.479(5)
O(1)−U(1)−O(1A)	180.0	O(1)−U(1)−O(3)	90
O(1A)−U(1)−O(3A)	90	O(1)−U(1)−O(3A)	90
O(1A)−U(1)−O(3)	90	O(1)−U(1)−N(1)	90
O(1A)−U(1)−N(1)	90	O(1A)−U(1)−N(1A)	90
O(1)−U(1)−N(1A)	90	O(1)−U(1)−O(4)	90
O(1A)−U(1)−O(4A)	90	O(1)−U(1)−O(4A)	90
O(1A)−U(1)−O(4)	90	O(3)−U(1)−O(3A)	180.0
O(3)−U(1)−N(1)	60.15(18)	O(3A)−U(1)−N(1)	119.85(18)
O(3A)−U(1)−N(1A)	60.15(18)	O(3)−U(1)−N(1A)	119.85(18)
O(3)−U(1)−O(4)	120.08(19)	O(3A)−U(1)−O(4A)	120.08(19)
O(3A)−U(1)−O(4)	59.92(19)	O(3)−U(1)−O(4A)	59.92(19)
N(1)−U(1)−N(1A)	180.0	N(1)−U(1)−O(4)	59.93(16)
N(1)−U(1)−O(4A)	120.07(16)	N(1A)−U(1)−O(4A)	59.93(16)
N(1A)−U(1)−O(4)	120.07(16)	O(4)−U(1)−O(4A)	180.0

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■ REFERENCES

(1) Suzuki, H.; Sasaki, Y.; Sugo, Y.; Apichaibukol, A.; Kimura, T. *Radiochim. Acta* **2004**, *92*, 463.

(2) Ansari, S. A.; Pathak, P. N.; Husain, M.; Prasad, A. K.; Parmar, V. S.; Manchanda, V. K. *Radiochim. Acta* **2006**, *94*, 307.

(3) Tian, G.; Zhang, P.; Wang, J.; Rao, L. *Solv. Extr. Ion Exch.* **2005**, *23*, 631.

(4) Sasaki, Y.; Choppin, G. *Radiochim. Acta* **1998**, *80*, 85.

(5) Babain, V. A.; Alyapyshev, M. Yu.; Kiseleva, R. N. *Radiochim. Acta* **2007**, *95*, 217.

(6) Lapka, J. L.; Paulenova, A.; Alyapyshev, M. Yu.; Babain, V. A.; Herbst, R. S.; Law, J. D. *Radiochim. Acta* **2009**, *97*, 291.

(7) Paulenova, A.; Alyapyshev, M. Yu.; Babain, V. A.; Herbst, R. S.; Law, J. D. *Sep. Sci. Technol.* **2008**, *43*, 2606.

(8) Romanovskiy, V. N.; Babain, V. A.; Alyapyshev, M. Yu.; Smirnov, I. V.; Herbst, R. S.; Law, J. D.; Todd, T. A. *Sep. Sci. Technol.* **2006**, *41*, 2111.

(9) Alyapyshev, M. Yu.; Babain, V. A.; Smirnov, I. V. *Radiochem. (Radiokhim. Engl. Ed.)* **2004**, *46*, 270.

(10) Alyapyshev, M. Yu.; Babain, V. A.; Smirnov, I. V.; Shadrin, A. Yu. *Czech. J. Phys.* **2006**, *56*, D469.

(11) Brayshaw, P. A.; Hall, A. K.; Harrison, W. T. A.; Harrowfield, J. M.; Pearce, D.; Shand, T. M.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *Eur. J. Inorg. Chem.* **2005**, 1127.

(12) Jain, S. L.; Slawin, A. M. Z.; Woollins, J. D.; Bhattacharyya, P. *Eur. J. Inorg. Chem.* **2005**, 721.

(13) Gonzalez-Baró, A. C.; Castellano, E. E.; Piro, O. E.; Parajón-Costa, B. S. *Polyhedron* **2005**, *24*, 49.

(14) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2004**, *43*, 2293.

(15) Goher, M. A. S.; Mautner, F. A.; Hafez, A. K.; Youssef, A. A. *Polyhedron* **2003**, *22*, 515.

(16) Tian, G.; Rao, L.; Teat, S. J. *Inorg. Chem.* **2009**, *48*, 10158.

(17) Marangoni, G.; Degetto, S.; Graziani, R.; Bombieri, G.; Forsellini, E. *J. Inorg. Nucl. Chem.* **1974**, *6*, 1787.

(18) Cousson, A.; Proust, J.; Rizkalla, E. N. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1991**, *47*, 2065.

(19) Cousson, A.; Nectoux, F.; Pagès, M.; Rizkalla, E. N. *Radiochim. Acta* **1993**, *61*, 177.

(20) Neu, M. P.; Johnson, M. T.; Matonic, J. H.; Scott, B. L. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **2001**, *57*, 240.

(21) Immirzi, A.; Bombieri, G.; Degetto, S.; Marangoni, G. *Acta Crystallogr., Sect. B: Struct. Sci.* **1975**, *31*, 1023.

(22) Masci, B.; Thuéry, P. *Polyhedron* **2005**, *24*, 229.

(23) Harrowfield, J. M.; Lugan, N.; Shahverdizadeh, G. H.; Soudi, A. A.; Thuéry, P. *Eur. J. Inorg. Chem.* **2006**, 389.

(24) Friese, J. I.; Nash, K. L.; Jensen, M. P.; Sullivan, J. C. *Radiochim. Acta* **2001**, *89*, 35.

(25) Ahmed, I. T.; El-Roudi, O. M.; Boraei, A. A. *J. Chem. Eng. Data* **1996**, *41*, 386.

(26) Choppin, G. R.; Rao, L. F. *Radiochim. Acta* **1984**, *37*, 143.

(27) Tian, G.; Rao, L.; Teat, S. J.; Liu, G. K. *Chem.—Eur. J.* **2009**, *15*, 4172.

(28) Sill, C.; Peterson, H. E. *Anal. Chem.* **1947**, *19*, 646.

(29) Gran, G. *Analyst* **1952**, *77*, 661.

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

(31) Martell, A. E.; Smith, R. M.; Motekaitis, R. J.; (Eds.): *Critically Selected Stability Constants of Metal Complexes, Database Version 8*; NIST Standard Reference Data: Gaithersburg, Maryland, 2004.

(32) Zanonato, P.; Di Bernardo, P.; Bismondo, A.; Liu, G.; Chen, X.; Rao, L. *J. Am. Chem. Soc.* **2004**, *126*, 5515.

(33) Gans, P.; Sabatini, A.; Vacca, A. *J. Solution Chem.* **2008**, *4*, 467.

(34) Grenthe, I.; Hansson, E. *Acta Chem. Scand.* **1969**, *23*, 611.

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

(36) Choppin, G. R.; Goedken, M. P.; Gritmon, T. F. *J. Inorg. Nucl. Chem.* **1977**, *39*, 2025.

(37) Jiang, J.; Renshaw, J. C.; Sarsfield, M. J.; Livens, F. R.; Collison, D.; Charnock, J. M.; Eccles, H. *Inorg. Chem.* **2003**, *42*, 1233.

(38) Ducommun, Y.; Helm, L.; Laurenczy, G.; Merbach, A. E. *Inorg. Chim. Acta* **1989**, 158.