

Selective Extraction of Uranium(VI) from Thorium(IV) Using New Unsymmetrical Acidic Phenanthroline Carboxamide Ligands

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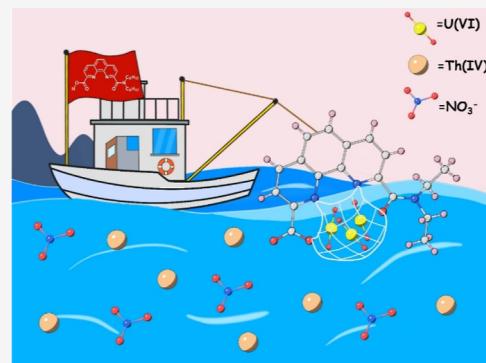
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ABSTRACT: In the thorium–uranium fuel cycle, ^{232}Th will produce fissional ^{233}U and radioactive ^{232}U simultaneously after irradiation. The selective separation of uranium from thorium-based spent fuel can enhance the utilization efficiency of nuclear fuel and promote the safety of nuclear energy utilization. In this work, a new type of unsymmetrical acidic phenanthroline carboxamide ligand represented as 9-(*N,N*-dialkylcarbamoyl)-1,10-phenanthroline-2-carboxylic acid (DEAPA and DOAPA) was synthesized for selective separation of U(VI) over Th(IV). The separation of small amounts of U(VI) from large amounts of Th(IV) could be achieved by using DOAPA to extract at high acidity (4 M HNO_3) and then using 1 M HNO_3 as the stripping agent. The complexation mechanism of these two ligands with U(VI) and Th(IV) was investigated through slope analysis, NMR spectrometric titration, UV–vis spectrophotometric titration, and single-crystal X-ray diffraction methods. Results from slope analysis and NMR spectrometric titration showed that DOAPA formed a 1:1 complex with U(VI) and formed 1:1 and 1:2 complexes with Th(IV). The larger stability constants ($\log \beta$) of 1:1 complexes of DEAPA/DOAPA with U(VI) than those with Th(IV) implied the stronger affinity of the ligands with U(VI), which was in good coincidence with the solvent extraction results. The crystal structures of the 1:1 complex of U(VI) and the two species of 1:1 and 1:2 complexes of Th(IV) with DEAPA were successfully analyzed by X-ray diffraction. This work provided a new type of unsymmetrical acidic phenanthroline carboxamide extractant for the efficient separation of U(VI) from Th(IV). The systematic study of the extraction and complexation behavior would be helpful to explore the effect of functional groups as well as design extractants with excellent performance.



INTRODUCTION

As a potential alternative to traditional fossil fuels, nuclear energy plays an important role in building a safe and reliable energy supply system and addressing climate change issues.^{1,2} The large-scale development of nuclear energy has raised higher demands for the supply of nuclear fuel.³ It has been widely reported that thorium is 3–4 times more abundant than uranium in the earth’s crust.^{4,5} The rich reserves of thorium and its military security have renewed the attention to thorium-based fuel.^{5,6} Compared with the traditional uranium-based fuel cycle, the thorium-based fuel cycle shows outstanding advantages including high conversion efficiency, less Pu and minor actinide production, and good inherent safety.⁷ Molten salt reactor (MSR) is regarded as the most ideal reactor system to realize the efficient utilization of thorium due to the possibility of online reprocessing and fuel breeding.⁸ The identification of MSR as one of the potential systems to achieve the Generation-IV goal will promote the development of thorium fuel cycle.⁹ Until now, Germany, the United States, the United Kingdom, India, China, etc., have

carried out fundamental research and preliminary small-scale application tests related to the thorium fuel cycle, systematically proving the possibility of using thorium as nuclear fuel in reactors.^{10–13} THTR-300 (Germany) and Fort St Vrain (USA) have achieved the production of 300 MWe power.¹⁴ India has been working on the thorium fuel cycle due to the large thorium deposit. Considerable experience is accumulated in the utilization of thorium in engineering-scale facilities under the guidance of the three-stage program.¹⁵ However, the significant challenges in the back end of the thorium fuel cycle restrict the industrial application of the thorium-based fuel cycle. The dissolution of thorium dioxide is more difficult than uranium oxide, so a small amount of HF addition to HNO_3 is

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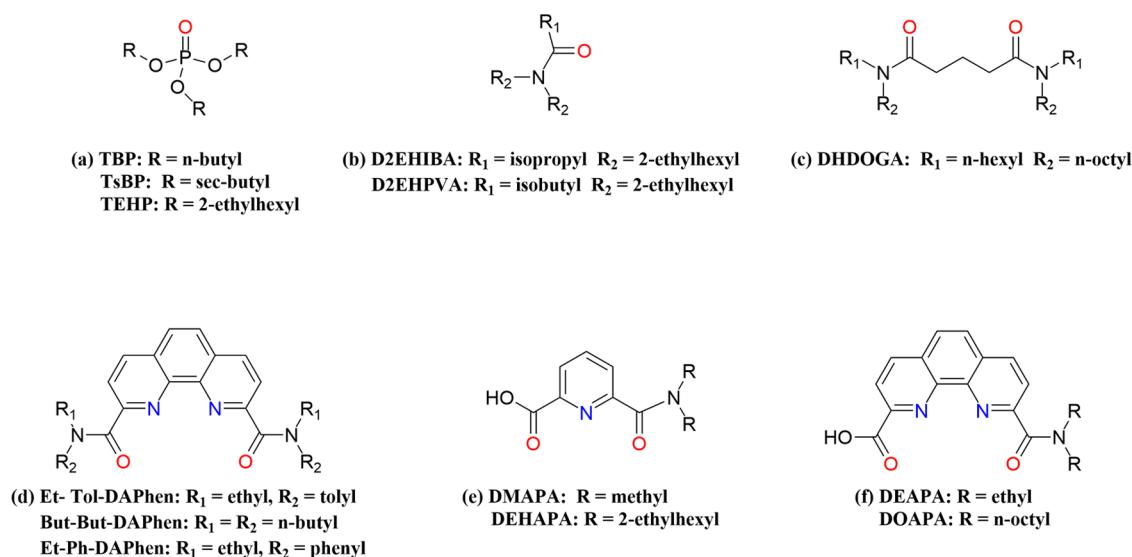


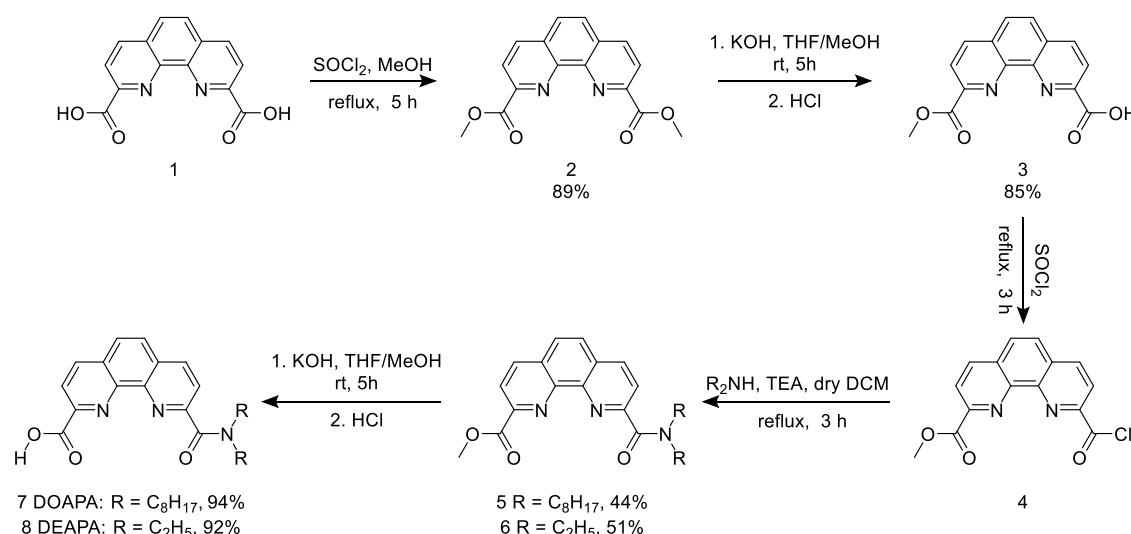
Figure 1. Ligands mentioned in this work.

necessary, which will enhance the corrosion of stainless steel equipment. The chemical separation of uranium from spent fuel is also difficult because of the stability and invariable oxidation state of thorium.¹⁶

²³²Th as a fertile material undergoes neutron capture reaction and subsequent beta decays to produce fissile ²³³U, which is also accompanied by the production of highly radioactive ²³²U in small amounts.^{16,17} For the bred ²³³U, the portion directly fissions in the reactor, while the nonfissional portion is removed from spent fuel and recycled as new fuel. Therefore, it is necessary to separate uranium from the irradiated thorium to enhance the utilization efficiency of thorium and reduce the volume of nuclear waste.¹⁸ The separation of highly radioactive ²³²U produced by irradiation will also help to achieve the safe utilization of nuclear energy. Unlike uranium/plutonium separation in the reprocessing of uranium-based spent fuel, the uranium/thorium separation is more challenging because of the invariable oxidation state of thorium.¹⁹ There has been extensive research in the separation of U(VI) and Th(IV), developing various technologies including solvent extraction,^{20,21} adsorption,^{22,23} ion exchange,²⁴ and so on, among which the solvent extraction method shows satisfactory performance because of the large processing capacity, high efficiency, and low cost. Until now, the Thorex (thorium–uranium extraction) process developed based on the Purex (plutonium uranium reduction and extraction) process is the only viable process to be applied in the industry, in which U(VI) and Th(IV) are coextracted by 5% tri-*n*-butyl phosphate (TBP) (Figure 1a) and then purified through ion exchange or precipitation.²⁵ The study on extractants possessing branched alkyl substituents such as tri-*sec*-butyl phosphate (TsBP)²⁶ and tris-2-ethylhexyl phosphate (TEHP)²⁷ has also been derived based on TBP. However, the organophosphorus extractants can only achieve the coextraction of U(VI) and Th(IV). In addition, the presence of phosphorus in the extractants will inevitably lead to secondary pollution because the extractants cannot be combusted completely. Therefore, *N,N*-dialkylamides consisting of only C, H, O, and N have been investigated due to their outstanding extraction performance and complete incinerability.^{28–32} The values of the separation factor ($SF_{U(VI)/Th(IV)}$)

for *N,N*-di-2-ethylhexylpivalamide (D2EHPVA) and *N,N*-di-2-ethylhexylisobutyramide (D2EHIBA) (Figure 1b) determined at 1 M HNO₃ were 2513 and 750, respectively, which were several orders larger than that of TBP ($SF_{U(VI)/Th(IV)} = 1.9$). However, the low distribution of U(VI) ($D_{U(VI)} < 5$, 6 M HNO₃) for D2EHPVA and D2EHIBA was insufficient for the efficient recovery of target elements from highly acidic spent fuel solutions.³³ Mowafy et al.³⁴ then applied glutaramide derivatives to the separation of U(VI) over Th(IV). An SF_{U(VI)/Th(IV)} value of 9.33 at 1 M HNO₃ was achieved by *N,N'*-dihexyl-*N,N'*-dioctylglutaramide (DHDOGA) (Figure 1c), whereas the highest $D_{U(VI)}$ by DHDOGA along the tested nitric acidic concentration was 3.18 ([HNO₃] = 3 M), remaining to be improved.

The extractants containing the highly preorganized phenanthroline skeleton exhibit outstanding advantages such as high extraction efficiency, fast kinetics, and strong acid resistance, which have been applied to the group separation of actinides over lanthanides from acidic solutions.^{35–37} The novel tetradentate ligand *N,N'*-diethyl-*N,N'*-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen) (Figure 1d) reported by Xiao et al.³⁸ exhibited strong extraction ability toward actinides with different oxidation states ($D_{Th(IV)} = 205$, $D_{U(VI)} = 25$, and $D_{Am(III)} = 6$, 1 M HNO₃). By tailoring the substitute groups in the diamide moieties, a series of ligands were synthesized and applied to the actinide extraction. The DAPhen ligands with different lengths of alkyl chains displayed lower $D_{U(VI)}$ than Et-Tol-DAPhen, but these ligands were still effective in U(VI) extraction. The $D_{U(VI)}$ values determined at 3 M HNO₃ were 118, 92, and 90 for But-But-DAPhen, Hex-Hex-DAPhen, and Oct-Oct-DAPhen, respectively.³⁹ In addition, DAPhen ligands (Et-Ph-DAPhen) also showed comparable extraction ability of Pu(IV) to U(VI) ($D_{Pu(IV)} = 42$ and $D_{U(VI)} = 56$, 4 M HNO₃).⁴⁰ Wang et al.⁴¹ synthesized four DAPhen ligands with asymmetric terminal groups *N,N'*-dialkyl substituent, among which *N,N'*-dimethyl-*N,N'*-dibutyl-2,9-diamide-1,10-phenanthroline gave the highest value of $D_{U(VI)}$ of 156.4 at 3 M HNO₃ ($SF_{U(VI)/Th(IV)} \approx 10$). The above results illustrate that although the extraction efficiency of U(VI) by phenanthroline-based extractants is high, the separation of U(VI) from tetravalent actinides such as Th(IV) and Pu(IV)

Scheme 1. Synthesized Routes of DEAPA and DOAPA Ligands

cannot be efficiently achieved. The existing phenanthroline-based extractants mostly present a symmetric structure with only one type of functional group. There has been little research investigating the extraction and complexation behavior of actinides with unsymmetrical phenanthroline-based extractants.

More recently, Wei et al.⁴² studied the complexation behavior of hexavalent actinides with dipicolinic acid derivatives 6-(dimethylcarbamoyl)picolinic acid (DMAPA) (Figure 1e) containing amide and carboxyl groups. The decreasing stability constants in the order of U(VI) > Np(VI) > Pu(VI) suggested the stronger affinity of DMAPA to U(VI). Xu et al.⁴³ then replaced the methyl group of DMAPA with the 2-diethylhexyl group to obtain a novel ligand 6-carboxylic di(2-ethylhexyl) amide pyridine (DEHAPA), which was proven to have a certain ability to separate U(VI) and Th(IV). However, the distributions of U(VI) and Th(IV) by DEHAPA were only 0.9 and 0.15 at 1 M HNO_3 , respectively, which was significantly lower than that of DAPhen. On the basis of the combination of carboxylic acid and amide, we tried to introduce the rigid phenanthroline skeleton into the extractant structure to obtain a new type of acidic phenanthroline carboxamide ligand 9-(N,N-diethylcarbamoyl)-1,10-phenanthroline-2-carboxylic acid (DEAPA) and 9-(N,N-diethylcarbamoyl)-1,10-phenanthroline-2-carboxylic acid (DOAPA) (Figure 1f). Taking advantage of the high preorganization and various functional groups, the novel extractants were supposed to have a strong extraction ability as well as separation ability. This was also the first time that a phenanthroline extractant possessing different functional groups (carboxylic acid and amide) was synthesized and investigated in the area of the separation of U(VI) and Th(IV). In this work, solvent extraction experiments for the separation of U(VI) and Th(IV) were performed for DEAPA and DOAPA in the *n*-octanol system. The complexation mechanism of DEAPA and DOAPA with U(VI) and Th(IV) was systematically investigated by slope analysis, NMR spectrometric titration, UV-vis spectrophotometric titration, and single-crystal X-ray diffraction methods.

EXPERIMENTAL SECTION

Chemicals. The uranyl(VI) nitrate, thorium(IV) nitrate, 1,10-phenanthroline-2,9-dicarboxylic acid, tetraethylammonium nitrate (Et_4NNO_3), and other chemical reagents were purchased from commercial approaches within analytical purity (AR) and were used without any further purification.

Synthesis. The synthesis route of DOAPA and DEAPA is shown in Scheme 1.^{38,44,45} The ^1H NMR spectra, ^{13}C spectra, and mass spectra of the compounds are provided in Figures S1–S5 (Supporting Information).

2,9-(Dimethoxycarbonyl)-1,10-phenanthroline (2). 1,10-Phenanthroline-2,9-dicarboxylic acid (1) (4.00 g, 15.02 mmol) was mixed with thionyl chloride (3 mL) in methanol (60 mL) at 0 °C. After heating and refluxing for 5 h, methanol was removed under reduced pressure to obtain a yellow solid. After being dissolved in dichloromethane, the organic product was successively washed with sodium bicarbonate solution and saturated sodium chloride solution and dried by anhydrous sodium sulfate. After the evaporation of solvent, the off-white solid (3.96 g, 89%) was acquired and directly used in the next step.

9-(Methoxycarbonyl)-1,10-phenanthroline-2-carboxylic Acid (3). The KOH (0.75 g, 13.37 mmol) methanol solution was added to the 2,9-(dimethoxycarbonyl)-1,10-phenanthroline (3.96 g, 13.37 mmol) in a THF/methanol (80/40 mL) mixture at 0 °C. After stirring for 5 h at ambient temperature, the solvent was removed under reduced pressure. The resulting yellow solid was suspended in water and acidified with excess dilute HCl to pH = 2. The precipitate was filtered and dried to afford the off-white solid (3.20 g, 85%).

9-(N,N-Dioctylcarbamoyl)-1,10-phenanthroline-2-methoxycarbonyl (5). 9-(Methoxycarbonyl)-1,10-phenanthroline-2-carboxylic acid (2.00 g, 7.09 mmol) was dissolved in thionyl chloride (50 mL) under argon protection. After the mixture was refluxed for 3 h, thionyl chloride was removed by vacuum distillation. Afterward, the remaining yellow solid was dissolved in overdried dichloromethane (50 mL) and cooled to 0 °C. Di-*n*-octylamine (5.13 g, 21.27 mmol) and triethylamine (4.30 g, 42.54 mmol) were added to the solution. The reaction continued to reflux for 3 h in an argon atmosphere. The organic layer was washed with a saturated sodium chloride solution and dried on anhydrous sodium sulfate. The solvent

was removed under vacuum. The crude product was chromatographed on silica gel (eluent: EA/PE = 3/1, v/v) to obtain 9-(*N,N*-dioctylcarbamoyl)-1,10-phenanthroline-2-methoxycarbonyl (1.42 g, 44%) as a brown oil.

DOAPA (7). The KOH (0.45 g, 8.01 mmol) methanol solution was added to 9-(*N,N*-dioctylcarbamoyl)-1,10-phenanthroline-2-methoxycarbonyl (1.35 g, 2.67 mmol) in a THF/methanol (46/23 mL) mixture. After stirring for 5 h at ambient temperature, the solvent was removed under reduced pressure. The resulting yellow solid was suspended in water and acidified with excess dilute HCl to pH = 2. The precipitate was filtered and dried to afford the white solid (1.23 g, 94%). ^1H NMR (500 MHz, DMSO): δ 8.67 (dd, J = 17.6, 8.3 Hz, 2H), 8.37 (d, J = 8.3 Hz, 1H), 8.18–8.12 (m, 2H), 7.92 (d, J = 8.2 Hz, 1H), 3.52–3.47 (m, 2H), 3.32–3.28 (m, 2H), 1.79–1.65 (m, 4H), 1.32 (dt, J = 33.8, 14.4 Hz, 11H), 0.98–0.92 (m, 2H), 0.87 (dt, J = 10.7, 6.6 Hz, 9H), 0.80–0.73 (m, 2H), 0.62 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, DMSO): δ 168.40, 167.00, 155.28, 149.07, 145.23, 144.47, 138.15, 138.06, 130.74, 129.11, 128.84, 127.56, 123.73, 122.86, 48.98, 45.95, 31.74, 31.37, 29.29, 29.15, 28.80, 28.51, 28.37, 27.72, 27.09, 26.48, 22.56, 22.16, 14.39, 14.21. ESI-MS(+): m/z = 492.3226 [L + H]⁺, m/z = 514.3041 [L + Na]⁺, and m/z = 538.2860 [L[−] + 2Na]⁺.

DEAPA (8). DEAPA was synthesized by substituting di-n-octylamine in the above procedures with diethylamine. DEAPA was obtained as a white powder and characterized by NMR and MS. ^1H NMR (500 MHz, DMSO): δ 8.69 (d, J = 8.3 Hz, 1H), 8.66 (d, J = 8.2 Hz, 1H), 8.37 (d, J = 8.3 Hz, 1H), 8.15 (t, J = 6.8 Hz, 2H), 7.97 (d, J = 8.2 Hz, 1H), 3.57 (q, J = 7.1 Hz, 2H), 3.36 (d, J = 7.0 Hz, 2H), 1.33 (t, J = 7.0 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, DMSO): δ 168.17, 167.02, 155.02, 149.07, 145.22, 144.45, 138.19, 130.70, 129.19, 128.83, 127.59, 123.70, 122.87, 43.65, 14.62, 13.31. ESI-MS(+): m/z = 323.1343 [L + H]⁺, 346.1161 [L + Na]⁺.

Solvent Extraction. The liquid–liquid extraction experiments were performed at 298 ± 1 K to test the ability of the ligands to separate U(VI) from Th(IV). The organic phases containing ligands with different concentrations were prepared by dissolving DEAPA/DOAPA in *n*-octanol. The aqueous phases were prepared by diluting a certain concentration of uranyl(VI) nitrate and thorium(IV) nitrate solutions to the required concentration. In a typical extraction experiment, 1 mL of the organic phase and 1 mL of the aqueous phase were added in a 10 mL centrifuge tube and then vigorously shaken with a vortex oscillator (2000 rpm/min, 10 min). After centrifugation (3000 rpm/min, 3 min) and phase separation, the concentrations of metal ions in the aqueous phase before and after extraction were determined by ICP–OES (730-ES, Varian Inc., Australia)/ICP–MS (Agilent Technologies 7800). The distribution ratio (*D*) and extraction efficiency (*E*) were calculated using the difference subtraction method, which is shown in the Supporting Information (eqs S1–S4).

Four agents, 1 M H₂SO₄, Na₂CO₃, HCl, and HNO₃ were selected for stripping experiments. The U(VI)/Th(IV)-loaded phase was obtained by contacting 10 mM DOAPA in *n*-octanol and a 4 M HNO₃ solution containing 0.5 mM U(VI) and Th(IV). 4 M HNO₃ was chosen to ensure the extraction efficiency of Th(IV), so that Th(IV) could be successfully loaded to the organic phase. The U(VI)/Th(IV)-loaded organic phases were then contacted with an equal volume of fresh stripping agents ($T = 298 \pm 1$ K, contact time = 10 min). Three stages of stripping were performed to investigate the stripping efficiency of these agents.

^1H NMR Spectrometric Titration. ^1H NMR spectroscopic titration is an effective method to monitor the species formed in the solution by analyzing the environment of the protons. In titration experiments, the 10 mM stock solutions of DOAPA, uranyl(VI) nitrate, and thorium(IV) nitrate were prepared by dissolving corresponding solid samples in CD₃OD/DMSO-*d*₆ (6/1, v/v). The mixed solvents were used to ensure the solubility of the complexes. The ligand and metal stock solutions were added into NMR tubes with an M/L ratio ranging from 0.0 to 2.0. The ^1H NMR spectra were recorded on an NMR spectrometer (Agilent DD2 600).

UV–Vis Spectrophotometric Titration. Spectrophotometric titration is a suitable method to determine the acid dissociation constants (pK_a), especially when the solubility of the sample is poor. In this work, DEAPA was used to determine the pK_a value of the acidic phenanthroline amide framework in water. The experiment was conducted on a Hitachi model UH-5300 spectrophotometer. DEAPA was neutralized to NaDEAPA with equimolar sodium hydroxide in beforehand and then dissolved in water to prepare 0.05 mM NaDEAPA stock solution, which was titrated with 1.5 mM HCl stock solution with an ionic strength of 0.01 M NaCl at 25 °C.

The complexation stability constants of U(VI) and Th(IV) with DOAPA and DEAPA were also determined by UV–vis spectrophotometric titrations. The 0.02 mM ligand stock solutions and 1.0 mM metal stock solutions were prepared by dissolving ligand and metal nitrate solids in HPLC acetonitrile, respectively. Meanwhile, 10 mM Et₄NNO₃ was added to control the ionic strength. An appropriate volume of metal stock solution was added to 2.5 mL of initial ligand solution in a quartz cell of 1.0 cm path length. The mixture was then stirred magnetically for 2 min to ensure that the complexation equilibrium was reached. The absorption spectra in the wavelength range of 240–380 nm were recorded after each titration until there was no significant change in the spectra. The stability constants were obtained on the base of these data using the *HyperSpec* program,^{46,47} which is an R package that allows effective handling of hyperspectral data encountered in Raman, UV–vis, IR, luminescence, etc. These data should be subject to the requirement that the spectral intensity of each chemical species is proportional to its concentration in solution.

Single-Crystal X-ray Diffraction Measurements. The single crystals of DEAPA with U(VI) and Th(IV) complexes were obtained by a solvent diffusion method. In the typical synthesis of the complex crystal, the metal nitrates and ligand with a molar ratio of 1:1 or 1:2 were dissolved in the methanol/water mixture (3/1, v/v). The solutions were filtered and then placed in an ether atmosphere. Single crystals were obtained after diffusion for a few days of diffusion. The X-ray crystallographic data were collected with Mo K α radiation ($\lambda = 0.71073$ Å; tube operating at 50 kV and 1.4 mA) with a Bruker D8 Venture diffractometer. The structure was solved and refined using Olex2.^{48–50}

■ RESULTS AND DISCUSSION

Solvent Extraction. DEAPA was found to be finitely soluble in water in the experiment. The UV–vis tests on the aqueous phase after extraction were performed to obtain quantitative results. The standard curves in Figure S6a prove that the absorbance is proportional to the species concentration in the solution following Lambert–Beer's law. There is

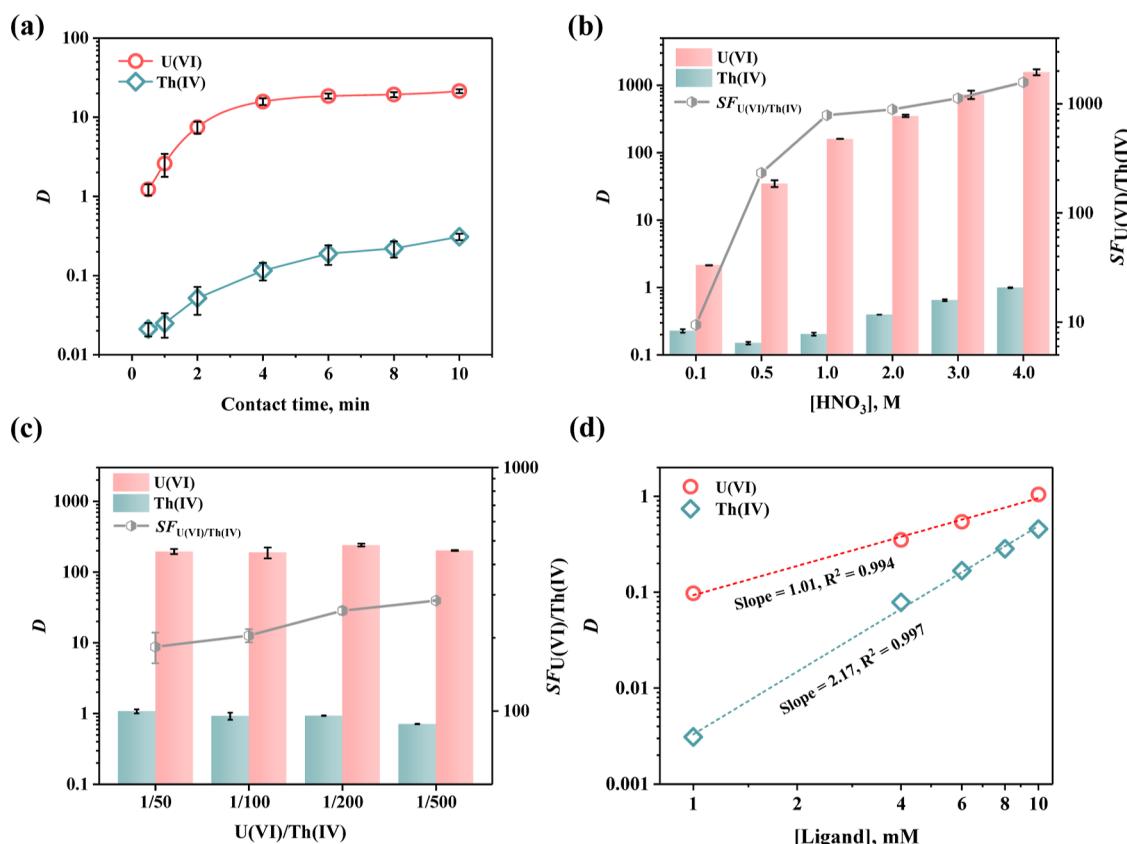


Figure 2. Distributions of U(VI) and Th(IV) by DOAPA as a function of (a) contact time ([ligand] = 10 mM, [U(VI)] = [Th(IV)] = 1 mM, and $[HNO_3]$ = 1 M). (b) HNO_3 concentration ([ligand] = 10 mM, [U(VI)] = [Th(IV)] = 1 mM, and contact time = 10 min). (c) Th(IV) concentration ([ligand] = 10 mM, [U(VI)] = 0.01 mM, and $[HNO_3]$ = 4 M). (d) Ligand concentration ([ligand] = 10 mM, [U(VI)] = [Th(IV)] = 0.01 mM, and contact time = 10 min).

an absorption peak in the UV-vis spectrum of the aqueous phase after contacting with the *n*-octanol phase containing 5 mM DEAPA (Figure S6b). The absorbance of the aqueous phase after dilution by 4 times is 0.859, from which we can deduce that around 2% of DEAPA will transfer to the aqueous phase during the extraction process. The small amount of transfer has little effect on extraction results.

The extraction properties of U(VI) and Th(IV) by DEAPA and DOAPA in *n*-octanol were investigated, and the results are shown in Figures 2 and S6. The distribution (D) of U(VI) and Th(IV) in 1 M HNO_3 as a function of contact time ranging from 0 to 10 min was tested to examine the extraction kinetics of the ligand. As displayed in Figures 2a and S6a, the U(VI) extraction equilibrium for DEAPA is achieved in 1 min, while no Th(IV) extraction is observed with the increasing contacting time under the condition of 1 M HNO_3 . As for DOAPA in Figure 2a, the U(VI) and Th(IV) extraction equilibrium is achieved in 4 and 6 min, respectively. The results prove that setting the extraction time as 10 min is enough to reach equilibrium.

The acidity of the aqueous phase can significantly influence the extraction of metal ions. Figures 2b and S6b show the influence of the HNO_3 concentration from 0.1 to 4 M on the distribution of metal ions using DOAPA and DEAPA in *n*-octanol. For DEAPA, the distribution of U(VI) initially decreases with the increasing HNO_3 concentration at low acidity (<1 M HNO_3) and then increases with further increasing HNO_3 concentration to 4 M, which is a typical pattern of acidic extractants such as *N,N*-di(2-ethylhexyl)-

diglycolamic acid (HDEHDGA).⁵¹ At low acidity, the ligand tends to lose a proton and extract metal ions through the ion-exchange mechanism.⁵² The pH of the aqueous phase containing 1 mM U(VI) with an initial pH of 1.13 decreases to 0.75 after the extraction, proving that the protons transfer from the organic phase to the aqueous phase. Instead, the ligand behaves as a neutral extractant to form a complex with metal ions and nitrates when the acidity is higher (>1 M HNO_3). The higher concentration of nitrate in the aqueous solution is beneficial for this process to proceed. Figure 2b shows that the distribution of U(VI) by DOAPA constantly increases with the HNO_3 concentration changing from 0.1 to 4 M. The $D_{U(VI)}$ values of DOAPA and DEAPA determined at 4 M HNO_3 are 1566 and 4, respectively. The stronger extraction ability of DOAPA is due to structural characteristics such as electron-donating ability and steric effect. On the one hand, the electron-donating ability of octyl is stronger than that of ethyl, resulting a higher electron density of the O atom of the amide group, which is beneficial for the complexation with metal ions. On the other hand, the metal ions in solution are surrounded by solvent molecules. The steric effect of a long alkyl chain can eliminate the solvent molecules around the metal ions to achieve desolvation, thus more easily to complex. Moreover, the longer alkyl chain of DOAPA allows the better dissolution of the ligand in the organic phase and higher interfacial activity, thus strengthening the extraction process. The high $SF_{U(VI)/Th(IV)}$ values for DOAPA ($SF_{U(VI)/Th(IV)} = 1582$, 4 M HNO_3) and DEAPA ($SF_{U(VI)/Th(IV)} = 24$, 4 M HNO_3) allow the ligands to selectively extract U(VI) from

Table 1. Stripping Percentage of U(VI) and Th(IV) by Investigated Agents^a

	1 M H ₂ SO ₄		1 M Na ₂ CO ₃		1 M HCl		1 M HNO ₃	
stripping times	U(VI)	Th(IV)	U(VI)	Th(IV)	U(VI)	Th(IV)	U(VI)	Th(IV)
1st	58.11	92.32	58.48	70.87	22.91	55.93	1.21	62.65
2nd	1.51	5.57	1.51	3.67	12.83	26.56	1.67	22.95
3rd	1.18	2.11	1.18	3.51	2.93	6.34	1.91	12.30
total	60.80	100.00	61.17	78.05	38.67	88.83	4.79	97.90

^a1 M H₂SO₄, 1 M Na₂CO₃, 1 M HCl, and 1 M HNO₃.

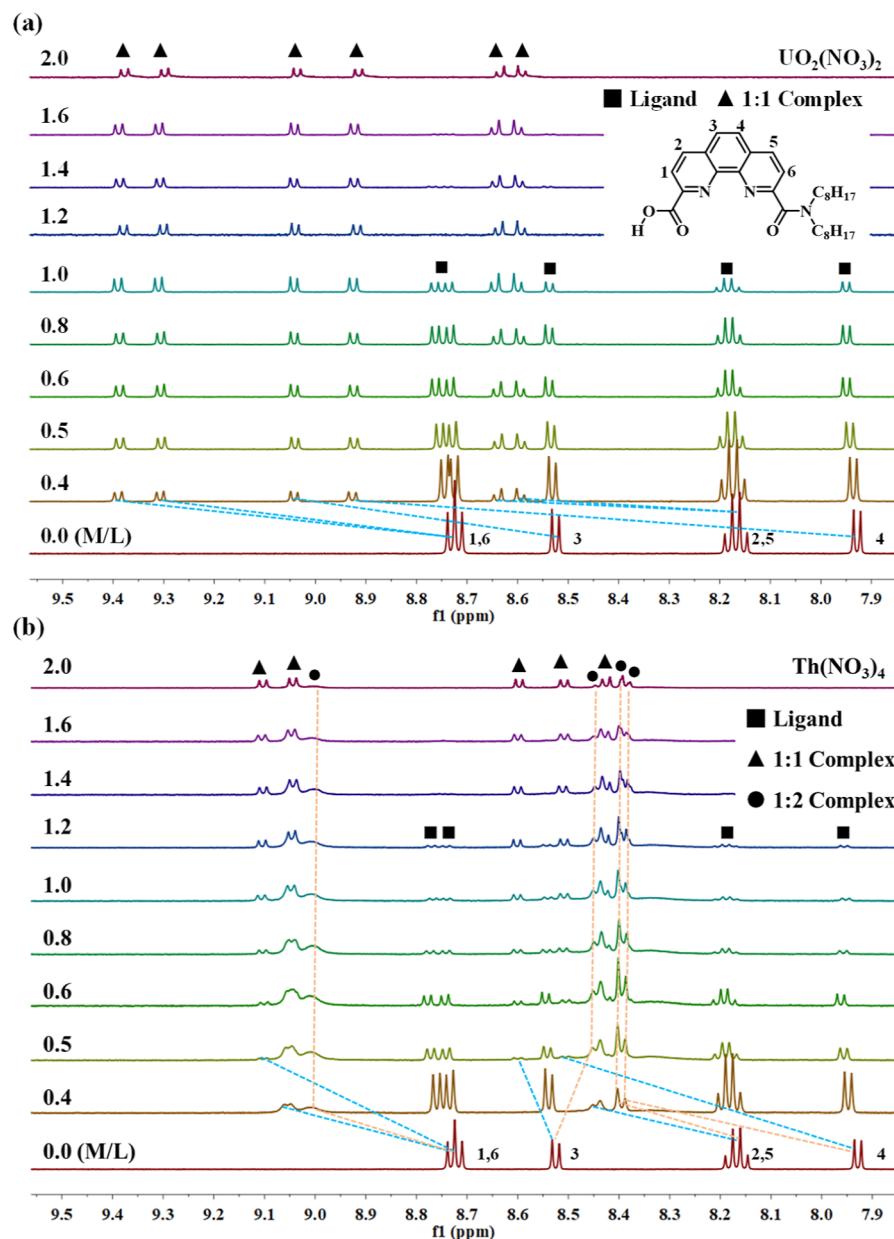


Figure 3. ¹H NMR spectra of DOAPA titrated with (a) UO₂(NO₃)₂ and (b) Th(NO₃)₄ in CD₃OD/DMSO-d₆ (v/v, 6/1). M/L denotes the metal-to-ligand molar equivalents.

acidic solutions in the range of HNO₃ concentration from 0.1 to 4 M.

Thorium-based spent fuel contains several fission products, among which lanthanides are present. To confirm the applicability of DOAPA, the extraction ability of Ln(III) (La(III), Eu(III), and Lu(III)) under acidic conditions was tested, and the results are shown in Figure S8. Contrary to

symmetric DAPhen ligands, DOAPA could hardly extract any Ln(III) from HNO₃ solutions, which proves the possibility of the selective extraction of U(VI) from spent fuel. Moreover, the separation of U(IV) in the presence of a large concentration of Th(IV) was investigated. The concentration of U(VI) was 1 ppm in the aqueous phase, and the concentration of Th(IV) was in the range of 50–500 times

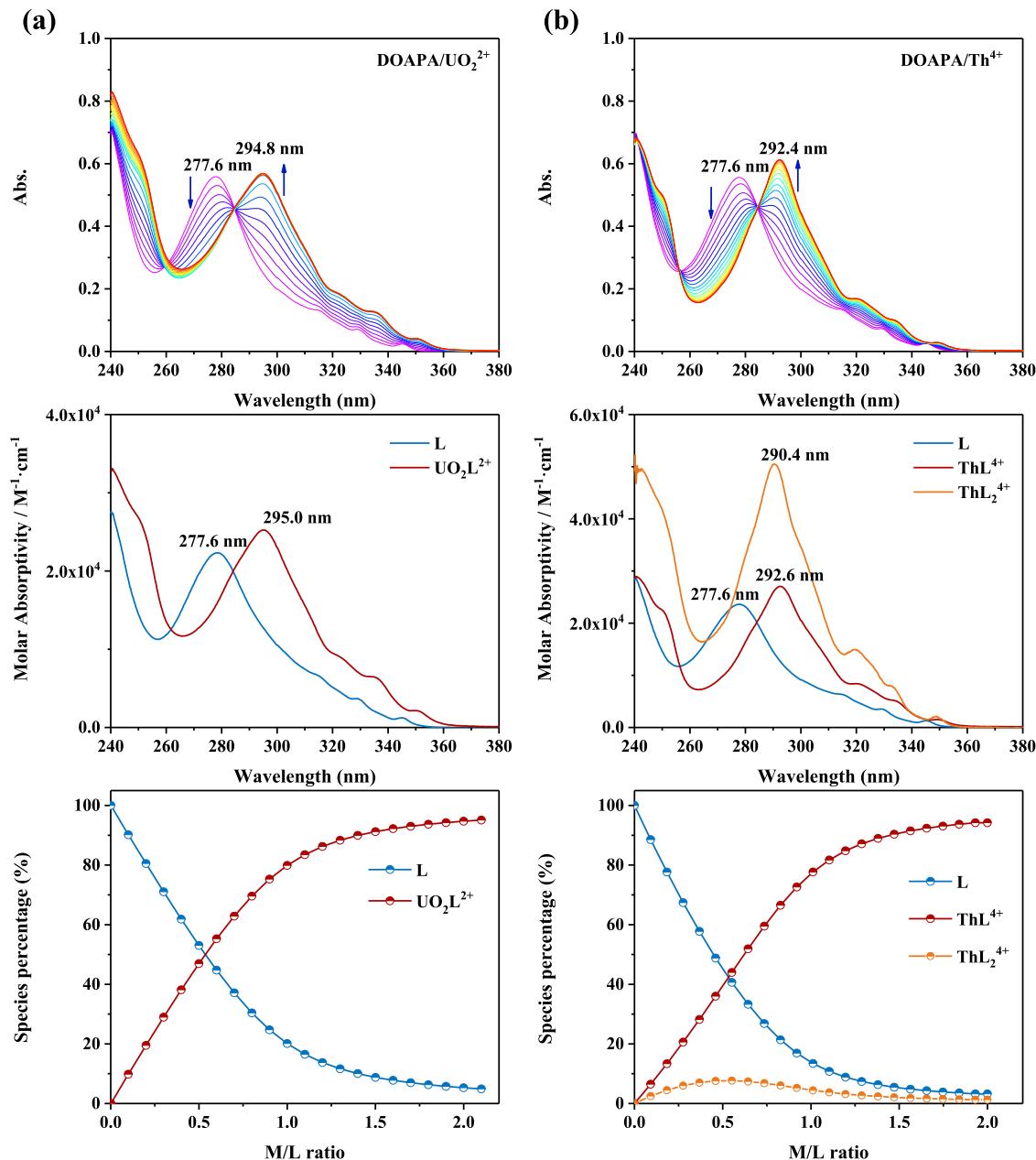


Figure 4. Spectrophotometric titrations of DOAPA complexing with (a) $\text{UO}_2(\text{NO}_3)_2$ ($C_L/C_{\text{U(VI)}} = 0.02 \text{ mM}/1 \text{ mM}$, a total of 0.105 mL of $\text{UO}_2(\text{NO}_3)_2$ solution was added) and (b) $\text{Th}(\text{NO}_3)_4$ ($C_L/C_{\text{Th(IV)}} = 0.02 \text{ mM}/1 \text{ mM}$, a total of 0.105 mL of $\text{Th}(\text{NO}_3)_4$ solution was added) in acetonitrile ($T = 298 \pm 1 \text{ K}$, $I = 0.01 \text{ M}$ Et_4NNO_3 , $V_0 = 2.5 \text{ mL}$). Top row: normalized absorption spectra. Middle row: molar absorptivity. Bottom row: species distribution curves.

of that of U(VI). As shown in Figure 2c, the value of $D_{\text{U(VI)}}$ increases slightly with the increase of Th(IV) concentration due to the salting out effect, whereas the value of Th(IV) shows a decreasing trend. This has also been observed in U(VI)/Th(IV) separation using TEHP.^{27,53} $\text{SF}_{\text{U(VI)}/\text{Th(IV)}}$ is determined to be 282 when the U(VI)/Th(IV) ratio in the aqueous phase is up to 1/500, proving that DOAPA has the potential to be applied under the Thorex feeding condition. To identify the stoichiometry of the ligand and metal ions, experiments using organic phases containing different concentrations of the ligand were conducted. As shown in Figure 2d, the slope values of $\log D_{\text{U(VI)}}$ and $\log D_{\text{Th(IV)}}$ versus $\log[\text{ligand}]$ are determined to be 1.01 and 2.17, respectively, which imply that there is one DOAPA molecule in the U(VI) complex and

two DOAPA molecules in the Th(IV) complex extracted to the organic phase.

The stripping efficiency is an important aspect in evaluating the performance of a novel extractant. Here, we tested the stripping efficiency of some common mineral acids (HCl , H_2SO_4 , and HNO_3) and Na_2CO_3 with a concentration of 1 M.⁵⁴ The loaded organic phase was obtained by equilibrating 10 mM DOAPA in *n*-octanol and 4 M HNO_3 solution containing 0.5 mM U(VI) and Th(IV). Three stages of stripping were performed between the loaded organic phase and fresh stripping agents, and then the concentration of metal ions was measured. As can be seen from Table 1, Th(IV) is much easier to be stripped than U(VI), suggesting that the complex formed by the ligand and U(VI) is steadier than

Table 2. Stability Constants ($\log \beta$) of the Complexation Reactions Determined by the UV–Vis Spectrophotometric Titration Method in CH_3CN at 298 K

ligand	metal ion	reaction	$\log \beta$	ionic medium	ref.
DEAPA	UO_2^{2+}	$\text{L} + \text{UO}_2^{2+} = \text{UO}_2\text{L}^{2+}$	6.41 ± 0.02	0.01 M Et_4NNO_3	p.w.
	Th^{4+}	$\text{L} + \text{Th}^{4+} = \text{ThL}^{4+}$	6.15 ± 0.02		
DOAPA	UO_2^{2+}	$2\text{L} + \text{Th}^{4+} = \text{ThL}_2^{4+}$	10.27 ± 0.13	p.w.	p.w.
	Th^{4+}	$\text{L} + \text{UO}_2^{2+} = \text{UO}_2\text{L}^{2+}$	6.91 ± 0.03		
Et-Et-DAPhen	UO_2^{2+}	$\text{L} + \text{Th}^{4+} = \text{ThL}^{4+}$	6.19 ± 0.01	p.w.	p.w.
	$2\text{L} + \text{Th}^{4+} = \text{ThL}_2^{4+}$	10.53 ± 0.05			
Oct-Oct-DAPhen	UO_2^{2+}	$\text{L} + \text{UO}_2^{2+} = \text{UO}_2\text{L}^{2+}$	4.07	0	39
PDA ^a	UO_2^{2+}	$\text{L} + \text{UO}_2^{2+} = \text{UO}_2\text{L}^{2+}$	4.02		
	UO_2^{2+}	$\text{UO}_2^{2+} + \text{L}^{2-} = \text{UO}_2\text{L}$	16.5		58,59

^aSolvent: water.

Th(IV). Among the four stripping agents, 1 M HNO_3 presents a high stripping selectivity to Th(IV). From the distribution data ($D_{\text{U(VI)}} = 1566$ and $D_{\text{Th(IV)}} = 0.99$) obtained under the condition of 4 M HNO_3 , it can be calculated that 99.93% of U(VI) can be extracted through one-stage extraction under the acidity of 4 M HNO_3 , while 49.75% of Th(IV) is entrained into the organic phase at the same time. By three-stage stripping with 1 M HNO_3 , 4.79% ($99.93 \% \times 4.79 \%$) of U(VI) and 49.19% ($50.25 \% \times 97.90 \%$) of Th(IV) are stripped. Therefore, 98.94% ($49.75 \% + 49.19 \%$) of Th(IV) remains in the aqueous phase, while 95.14% of U(VI) is in the organic phase. When the molar ratio of U(VI) and Th(IV) is 1:100 in the feed solution, the purity of Th(IV) can be increased from 99.01 to 99.95% after the foresaid extraction and stripping process, with only 1.06% loss of Th(IV). The good separation of small amounts of U(VI) from large amounts of Th(IV) can be achieved through more cycles of extraction stripping.

¹H NMR Spectrometric Titration. Having studied the extraction performance of the ligands, various experimental methods were adopted to investigate the complexation mechanism of the ligands with metal ions to establish the structure–activity relationship of ligands. NMR titration is commonly used to identify the stoichiometry of the complex of ligands with metal ions.⁵⁵ Figure 3 displays the NMR results of the solutions containing different ratios of DOAPA and metal ions. Due to the poor solubility of U(VI) and Th(IV) complexes in single-solvent CD_3OD , $\text{DMSO}-d_6$ was added to improve the solubility of the complexes.

As shown in Figure 3a, the intensity of four well-distinguished peaks (■) corresponding to the six hydrogens on the phenanthroline ring of DOAPA gradually declines with the addition of a U(VI) solution. The original triple peak at 8.75 ppm of the ligand splits into two doublets at 8.76 and 8.80 ppm. Meanwhile, new peaks (▲) appear at 8.61, 8.65, 8.94, 9.05, 9.32, and 9.41 ppm, whose intensity constantly increases with the increase of M/L ratio. As the M/L ratio exceeds 1.0, the peaks of ligands disappeared, and only the 1:1 U(VI)/DOAPA complex exists in the system. The quantitative complexation between DOAPA with U(VI) also proves the strong complexation ability of DOAPA. In the titration results of Th(IV) shown in Figure 3b, the newly generated peaks display different changing trends along the titration. The intensity of peaks marked as ● increases to maximum at M/L = 0.6 and then constantly decreased until M/L = 2.0, while the intensity of the peak marked as ▲ keeps enhancing, indicating that two different types of complexes exist in the solution. The signal ● and ▲ represents a 1:2 and 1:1 Th(IV)/DOAPA

complex, respectively. The peaks of two complexes coexist in the system when the M/L ratio changes from 0.4 to 2.0. This can be further proved by the following single-crystal structure analysis. These results prove that DOAPA complexes with U(VI) in 1:1 stoichiometry, while it complexes with Th(IV) in 1:1 and 1:2 stoichiometry, which is in agreement with those obtained by slope analysis.

UV–Vis Spectrophotometric Titration. In this work, DEAPA was used to determine the pK_a value of the acidic phenanthroline amide framework in water. The pK_a value of DEAPA was estimated to be 3.88 in water by fitting the titration data displayed in Figure S9. The acidity of DEAPA is weaker than that of DGAA ($\text{pK}_a = 3.54$)⁵⁶ and CPCP ($\text{pK}_a = 3.24$).⁴² The stability constants ($\log \beta$) of the ligands with U(VI) and Th(IV) were obtained through UV–vis spectrophotometric titration.^{46,57} The normalized absorption spectra, molar absorptivity, and species distribution curves are shown in Figures 4 and S10. As shown in the top row of Figure 4a,b, the absorption curves of DOAPA in the range 240–380 nm change significantly along the titration process. With the addition of U(VI) or Th(IV) solution, the ligand peak at 277.6 nm weakens, while a new peak appears at 294.8 or 292.4 nm and enhances gradually. The isosbestic point at around 282.5 nm indicates that there is more than one species in the solution. DEAPA titrations in Figure S9a,b provide similar results. The new peaks with the addition of U(VI) or Th(IV) solution appear at 295.2 or 292.0 nm.

The simulation results using HyperSpec show that the titration data of U(VI) and Th(IV) fit well with different models. The stability constants of the complex of the ligands with U(VI) and Th(IV) are listed in Table 2. The value of the stability constant of the 1:1 complex of DOAPA with U(VI) (6.90 ± 0.03) is about 0.7 orders of magnitude larger than that of the 1:1 complex of DOAPA with Th(IV) (6.19 ± 0.01). A slighter difference is found in $\log \beta$ values between the 1:1 complex of DEAPA with U(VI) (6.41 ± 0.02) and Th(IV) (6.15 ± 0.02). The results illustrate that the ligands (DOAPA and DEAPA) have stronger affinity toward U(VI) than Th(IV), thus enabling highly selective extraction of U(VI) over Th(IV) in solvent extraction experiments. The values of the second-step constants ($\log k_2 = \log \beta_2 - \log \beta_1$) of the complex of the ligands with Th(IV) are significantly lower than that of first-step constants ($\log k_1 = \log \beta_1$). The species distribution curves also reflect this property through the fact that the maximum ratio of the 1:2 complex is less than 10%. Similar UV–vis results have been reported in the previous study of DAPhen ligands.⁴¹ The probable reason is that the nitrates participate in coordination, which would compete with

the second ligand. The reported stability constants of 1:1 complex of Et-Et-DAPhen and Oct-Oct-DAPhen with U(VI) in acetonitrile were 4.07 and 4.02,³⁹ lower than that of the 1:1 complex of the corresponding unsymmetrical ligands. The $\log \beta$ of the 1:1 complex of PDA with U(VI) displayed a rather high value of 16.5 ($I = 0$).^{58,59} The values of $\log \beta$ become smaller as the ligand structure changes from PDAM (two carboxylic groups) to DEAPA/DOAPA (one carboxylic group and one amide group) and Et-Et-DAPhen/Oct-Oct-DAPhen (two amide groups). The study of oxa-diamide and related ligands provides the same results.⁶⁰ The trends imply that the introduction of a carboxylic acid group can provide a stronger complexation ability than an amide group, which is owing to the electrostatic interaction between the carboxylate group and metal ions. However, introducing carboxylic acid groups into both sides of phenanthroline would reduce the solubility of the ligand in organic solvents, impeding its application in extraction. The unsymmetric ligands in this work designed by combining a carboxylic acid group and an amide group could feature the goodness of strong complexation ability and good solubility. These results would be helpful in the design of novel ligands with high extraction efficiency.

Structures of Complexes in the Solid State. Due to the flexible characteristic of the DOAPA ligand, we used the DEAPA (HL) ligand with a short alkyl chain to grow single complex crystals. The UV-vis titration results have proved that the coordination mode of DEAPA and DOAPA with the metal ions is similar; DEAPA could be used as a representative ligand for single-crystal cultivation therefore. The crystals of the complex of DEAPA with U(VI) and Th(IV) were obtained using an ether diffusion method and then analyzed with an X-ray diffraction technique to reveal the complex mechanism at the molecular level. The structural refinement parameters and the crystal data for the complexes are listed in Tables S1–S3.

The structure and coordination mode of the 1:1 complex of DEAPA with U(VI) are shown in Figure 5a,b. In the

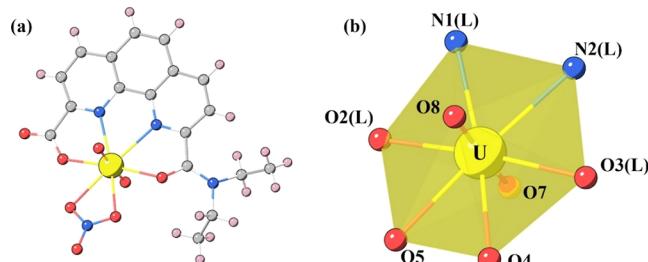


Figure 5. (a) Single-crystal structure of $[UO_2LNO_3]$ and (b) coordination mode of U(VI) in $[UO_2LNO_3]$. Yellow, red, blue, gray, and pink represent the U, N, C, and H atoms, respectively.

$[UO_2LNO_3]$ complex, the ligand is tetradentate-coordinated with the center metal ion through the two N atoms of the phenanthroline skeleton, one O atom of the amide group, and one O atom from the carboxylic acid group. Additionally, a nitrate ion is bound to U(VI) from the opposite side of the phenanthroline almost on the phenanthroline equatorial plane. This could be illustrated by the angles of N1–U1–O4 (171.67°) and N2–U–O5 (173.86°). The geometry of the eight-coordinated U(VI) displays a distorted hexagonal-bipyramidal structure (Figure 5b), which is commonly observed in U(VI) complexes such as $[UO_2(DMAPA)_2]$ and $[(UO_2)_2(O_2)(TMPhenDA)_2](ClO_4)_2$.^{42,61} The selected bond

length is given in Table 3. The bond lengths of U(VI)–N1 (2.58 Å) and U(VI)–O2 (2.33 Å) are shorter than those of

Table 3. Selected Bond Distances (Å) Associated with the Central Metal Ion in Complexes

	$[UO_2LNO_3]$	$[ThL(NO_3)_4]^-$	$[ThL_2(H_2O)_2]^{2+}$
coordination number (CN)	8	12	10
M–O _{COOH} /Å	2.3331(17)	2.428(3)	2.411(3)
M–O _{amide} /Å	2.4385(17)	2.493(3)	2.438(3)
M–N _L ^a /Å	2.580(2)	2.635(3)	2.657(4)
M–N _L ^b /Å	2.614(2)	2.689(3)	2.715(4)

^aDenotes the N donor atom of the phenanthroline near the carboxylic group. ^bDenotes the N donor atom of the phenanthroline near the amide group.

U(VI)–N2 (2.61 Å) and U(VI)–O3 (2.44 Å), respectively, implying that the central U(VI) is more inclined toward the carboxylic acid moiety of the ligand in the coordination sphere. The optimized structure of $[UO_2(Et-Et-DAPhen)NO_3]^+$ displayed a similar coordination mode with $[UO_2LNO_3]$.⁶² Compared with the calculated U(VI)–N(L) (2.646 Å) and U(VI)–O(L) (2.417 Å) bond lengths in the complex $[UO_2(Et-Et-DAPhen)NO_3]^+$, the corresponding bond lengths in the $[UO_2LNO_3]$ complex are shorter. The results indicate that the coordination ability of the carboxylic acid group is stronger than that of the amide group, which also mirrors the results of UV-vis titration that examines the higher value of $\log \beta$ of acidic phenanthroline carboxamide (DOAPA and DEAPA) than that of the corresponding diamide ligands. The average length of U(VI)–N(L) and U(VI)–O(L) is 2.597 and 2.386 Å, proving that the hard O atom has stronger affinity to U(VI).

The complex of DEAPA with Th(IV) obtained in the experiment contains the $[ThL(NO_3)_4]^-$ anion and $[ThL_2(H_2O)_2]^{2+}$ cation with different coordination numbers, which has also been reported in the thorium complex $[Th(NO_3)_3(dchso)_4][Th(NO_3)_5(dchso)_2]$.⁶³ As shown in Figure 6, the central Th(IV) in $[ThL(NO_3)_4]^-$ is 12-coordinated with two N atoms from phenanthroline, one atom from carboxylic acid, one atom from amide, and eight atoms from four nitrates (Figure 6a). In the structure of $[ThL_2(H_2O)_2]^{2+}$, the central Th(IV) is 10-coordinated with four N atoms from phenanthroline, two O atoms from carboxylic acid, two O atoms from amide, and two O atoms from two water molecules (Figure 6b). The same coordination number was also obtained in the 1:2 complex of Th(IV) with the symmetric DAPhen ligand (TMPhenDA).⁶⁴ Different from that in $[ThL(NO_3)_4]^-$, Th(IV) in $[ThL_2(H_2O)_2]^{2+}$ lies out of the plane of the DEAPA ligand, which is similar to the structure of $[Th(PDA)_2(H_2O)_2]$.⁶⁵ The bigger coordination number of Th(IV) compared to that of U(VI) allows more small molecules such as NO_3^- and H_2O to participate in the coordination sphere, which would improve the water solubility of the complex. As displayed in (Figure 6c), $[ThL_2(H_2O)_2]^{2+}$ is connected with two $[ThL(NO_3)_4]^-$ through a hydrogen bond (1.823 Å) to form an electrically neutral repeating unit $[(ThL_2(H_2O)_2)(ThL(NO_3)_4)]$. The selected bond lengths of $[ThL(NO_3)_4]^-$ and $[ThL_2(H_2O)_2]^{2+}$ are listed in Table 3. The corresponding M–O(L) and M–N(L) bonds in U(VI) complexes are shorter than that in Th(IV) complex, proving that the interaction between the ligand and U(VI) is stronger.

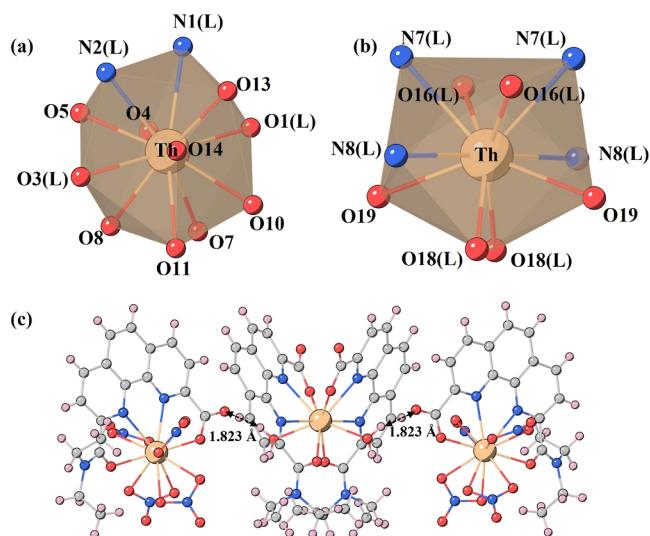


Figure 6. (a) Coordination mode of Th(IV) in $[\text{ThL}(\text{NO}_3)_4]^-$; (b) coordination mode of Th(IV) in $[\text{ThL}_2(\text{H}_2\text{O})_2]^{2+}$; and (c) single-crystal structure of $[(\text{ThL}_2(\text{H}_2\text{O})_2)(\text{ThL}(\text{NO}_3)_4)_2]$. Orange, red, blue, gray, and pink represent the Th, O, N, C, and H atoms, respectively.

CONCLUSIONS

In this work, two new unsymmetrical acidic phenanthroline carboxamide ligands designed based on the hard–soft combination strategy were applied to the extraction of U(VI) from Th(IV) in nitric acid solutions. Both DEAPA and DOAPA show satisfactory performance in efficiency, selectivity, kinetics, and stripping, while DOAPA ($D_{\text{U(VI)}} = 1566$ and $SF_{\text{U(VI)/Th(IV)}} = 1582$, 4 M HNO₃) gives higher $D_{\text{U(VI)}}$ values than DEAPA due to its stronger hydrophobicity. The experimental scheme of high-acidity extraction and low-acidity stripping can efficiently and easily achieve the separation of U(VI) and Th(IV). The results of slope analysis and spectroscopy titration studies consistently prove that the ligands complex with U(VI) in 1:1 stoichiometry while complex with Th(IV) in 1:1 and 1:2 stoichiometry. The simulated log β further reflects the stronger complexation ability of the ligands to U(VI) than Th(IV). The single crystal structure studies show that U(VI) is eight-coordinated with L to form the $[\text{UO}_2\text{LNO}_3]$ complex, while in the complex $[(\text{ThL}_2(\text{H}_2\text{O})_2)(\text{ThL}(\text{NO}_3)_4)_2]$, Th(IV) has two different coordination numbers of 12 and 10. The investigation of the coordination mechanism proves that the ligands have stronger complexation ability to U(VI), which can well explain the higher extraction efficiency of the ligands to U(VI). This work provides a type of promising ligand suitable for the selective extraction of small amounts of U(VI) over large amounts of Th(IV), which is of great significance to improve the utilization efficiency of nuclear fuel and promote the safety of thorium-based fuel cycle.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.3c02101>.

¹H NMR spectra, ¹³C NMR spectra, and mass spectra of the ligands; calculation equations used in solvent extraction; additional UV-vis spectrophotometric data;

structural refinement parameters; and crystal data for the complexes (PDF)
Structural refinement parameters of $[(\text{ThL}_2(\text{H}_2\text{O})_2)(\text{ThL}(\text{NO}_3)_4)_2]$ (CIF)
Structural refinement parameters of UO_2LNO_3 (CIF)

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Author Contributions

S.W. and X.Y. contributed equally to this work. Shihui Wang contributed to conceptualization, investigation, data curation, formal analysis, and writing—original draft. Xiaofan Yang contributed to methodology and writing—review and editing. Lei Xu contributed to writing—review and editing. Yujie Miao contributed to formal analysis. Xiao Yang contributed to methodology. Chengliang Xiao contributed to conceptualization, supervision, and funding acquisition.

Notes

The authors declare no competing financial interest.

Biography



Chengliang Xiao graduated from Zhejiang University with a PhD degree in 2011 and successively worked at Purolite (China) Co. Ltd, Institute of High Energy Physics (CAS), Soochow University, and

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