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Influence of a N-Heterocyclic Core on the Binding Capability of N,O-Hybrid Diamide Ligands toward Trivalent Lanthanides and Actinides

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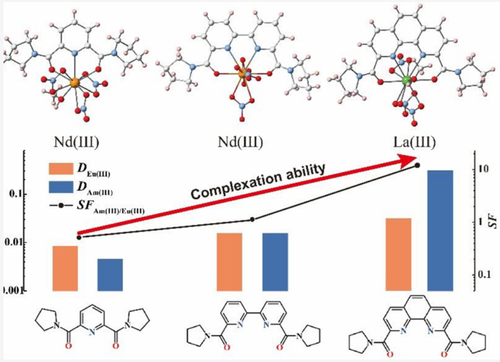

ABSTRACT: N,O-hybrid diamide ligands with N-heterocyclic skeletons are one of the promising extractants for the selective separation of actinides over lanthanides in a highly acidic HNO_3 solution. In this work, three hard−soft donor mixed diamide ligands, pyridine-2,6-diylbis(pyrrolidin-1-ylmethanone) (Pyr-PyDA), 2,2′-bipyridine-6,6′-diylbis(pyr-rolidine-1-ylmethanone) (Pyr-BPyDA), and (1,10-phenanthroline-2,9-diyl)bis(pyrrolidin-1-ylmethanone) (Pyr-DAPhen), were synthesized and used to probe the influence of N-heterocyclic cores on the complexation and extraction behaviors with trivalent lanthanides and actinides. ^{1}H NMR titration experiments demonstrated that 1:1 metal-to-ligand complexes were mainly formed between the three ligands and lanthanides, but 1:2 type complexes were also formed between tridentate Pyr-PyDA and Lu(III). The stability constants (log β) of these three ligands with two typical lanthanides, Nd(III) and Eu(III), were determined through spectrophotometric titration. It is found that Pyr-DAPhen formed the most stable complexes, while Pyr-PyDA formed the most unstable complexes with lanthanides, which coincided well with the following solvent extraction results. The solid-state structures of 1:1 type complexes of these three ligands with La(III), Nd(III), and Er(III) in nitrate media were identified by a single-crystal X-ray diffraction technique. Nd(III) and Er(III) were 10-coordinated with Pyr-PyDA, Pyr-BPyDA, and Pyr-DAPhen via one ligand molecule and three nitrate ions. La(III), because of its larger ionic radius, was 11-coordinated with Pyr-DAPhen through one ligand molecule, three nitrate ions, and one methanol molecule. Solvent extraction experiments showed that the preorganized phenanthroline-derived Pyr-DAPhen had the best extraction performance for trivalent actinide among the three ligands tested. This work provides some experimental insights into the design of more efficient ligands for trivalent actinide separation by adjusting the N-heterocyclic cores.

■ INTRODUCTION

Nowadays, nuclear power, which has low or even no carbon dioxide emissions, has become an effective strategy to deal with the energy crisis and climate change.[1,2] However, one significant shortcoming of nuclear energy is the need to dispose of the spent nuclear fuel (SNF)[3,4] generated from nuclear plants. Although most of the U and Pu in SNF can be recycled through the PUREX process,[5,6] the most problematic nuclides, that is, long-lived and highly radioactive minor actinides[7,8] (MAs) like Am(III) and Cm(III), still contain PUREX raffinate (so-called highly active liquid waste).[4] The currently most advanced and effective strategy to solve this problem is the “partition and transmutation”[4,9,10] (P&T) strategy, whose core idea is to covert those long-lived and highly radioactive nuclides into short-lived or stable nuclides by the neutron-induced nuclear transmutation reaction.[11] Notably, the progress of transmutation of MAs can be seriously hindered by the lanthanide isotopes because of their high neutron absorption cross section. Therefore, the lanthanides must be separated from the actinides prior to transmutation.[4,6,12] However, because of the very similar coordination chemical properties between trivalent lanthanides and actinides in aqueous solution,[13−15] the chemical separation of trivalent actinides over lanthanides from highly active nuclear waste is very challenging and thus becomes a key step for the P&T[9,16] strategy.

However, on the basis of the hard−soft acid−base theory, trivalent actinide ions are relatively softer than lanthanide ions and are inclined to form more stable covalent complexes with softer N- or S-donor ligands.[1,17−23] Therefore, the highly efficient separation of trivalent actinides over lanthanides can be achieved using those N- or S-donor ligands, and various kinds of extractants for the separation of trivalent lanthanides

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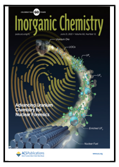

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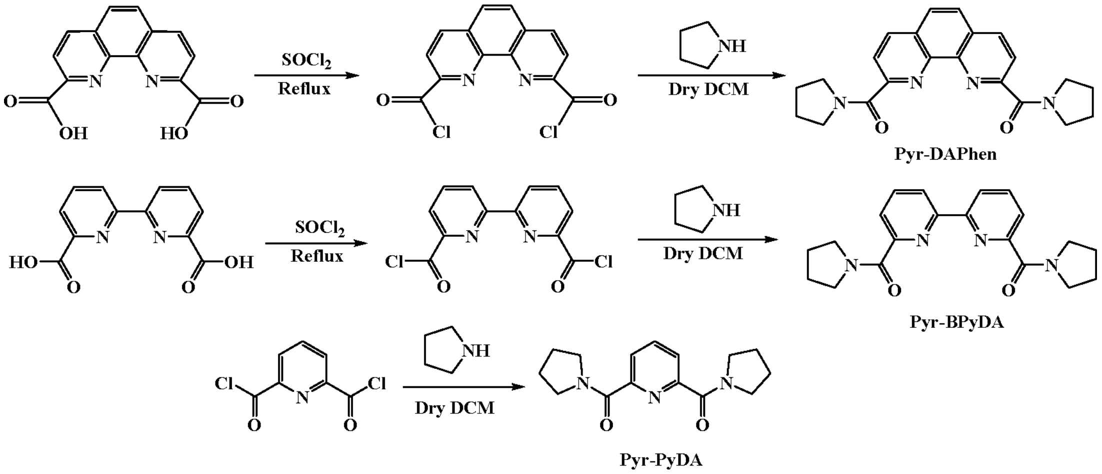

Figure 1. Synthesis routes of the Pyr-DAPhen, Pyr-PyDA, and Pyr-BPyDA ligands.

and actinides have been developed.[24−29] Compared with S-containing ligands, those N- and/or O-donor ligands only contain C, H, O, and N elements (the so-called CHON principle)[12,30] are completely incinerable and would produce much less solid radioactive waste during the solvent extraction process and thus became the more ideal extractants for the separation of trivalent actinides over lanthanides.[19,31,32]

Among the N-donor ligands studied, the triazinylpyridine ligand is one of the most promising actinide-selective extractants. The first developed was 2,6-bis(5,6-dialkyl-1,2,4-triazinyl)pyridine (BTP),[33,34] like CyMe$_4$-BTP,[35] but it was found that, because of the very high extraction ability of CyMe$_4$-BTP toward trivalent actinides ($D_{Am}/D_{Eu} > 1000$), the stripping of extracted Am(III) was very difficult.[33,36] To improve the back-extraction problem, a type of tetradentate ligand, 6,6′-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2′-bipyridine (BTBP),[37] was developed. However, the extraction rates of BTBP-type ligands for actinides were relatively slow.[5,20,38] In order to overcome this shortcoming, a type of preorganized phenanthroline-derived ligand, 2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-1,10-phenanthroline (BTPhen),[20] was developed. As was reported that CyMe$_4$-BTPhen exhibited a very strong selective extraction ability and fast extraction rates for Am(III) over Eu(III) ($D > 1000$; separation factor $SF_{Am/Eu} > 200$) in a highly acidic HNO_3 solution.[5,21,22,29] Thus, we can see that in these triazine-type ligands the N-hetercyclic cores have a huge impact on the separation of actinides over lanthanides.[20,22,39,40] Additionally, it was reported that the amide ligands with rigid phenanthroline skeletons had a stronger extraction ability and higher selectivity toward trivalent actinides over lanthanides compared with pyridine- or bipyridine-skeleton-based amide-type ligands.[21,41−44] With the introduction of an amide group into the ligands, the carbonyl moiety can promote ligand coordination with the lanthanides and greatly weaken the protonation reaction of the ligands. The $D_{Eu(III)}$ values are in the range from 2 to 20 for pyridine-derived *N*-methyl-*N*-phenyl-2-(1*H*-benzimidazol-2-yl)pyridine-6-carboxamide, and $D_{Eu(III)}$ varies from 0.01 to 0.2 for 2-(2-pyridyl)-benzimidazole.[26] Meanwhile, both soft N and hard O donors take part in the complexation with metal ions, in which the "hard" O donors provide high distribution ratio values and the "soft" N donors form stronger complexes with actinides. For example, the $SF_{Am/Eu}$ values of the bipyridine-derived diamides of 2,2′-dipyridyl-6,6′-dicarboxylic acid are in the range of 1−19.[43] Also N,O-hybrid phenanthrolinediamide-type ligands, like *N*,*N*′-diethyl-*N*,*N*′-ditolyl-2,9-diamide-1,10-phenanthroline,[21] have demonstrated remarkable separation for actinide ions ($SF_{Th(IV)/Eu(III)}$, $SF_{U(VI)/Eu(III)}$, and $SF_{Am(III)/Eu(III)} = 2277$, 277, and 67 in 1.0 M HNO_3, respectively).[26,45−47] In brief, for those amide-type ligands, their complexation and extraction selectivity of actinides over lanthanides can also be tuned by adjusting their N-heterocyclic cores because the central cores can control the rigidity of the ligands and have a significant impact on their complexation properties toward trivalent actinides and lanthanides.[45,48−51] This assertion was also confirmed previously using density functional theory (DFT) calculations.[52] However, the corresponding detailed experimental investigations about the influence of a N-heterocyclic core on the complexation properties of N,O-hybrid diamide ligands toward trivalent lanthanides and actinides have not been comparatively reported.

The purpose of this work is to provide some new insights into the influence of a N-heterocyclic core on the binding capability of N,O-hybrid diamide ligands toward trivalent lanthanides and actinides experimentally. To further explore the structure−activity relationship, we synthesized three N-heterocyclic diamide ligands, Pyr-PyDA, Pyr-BPyDA, and Pyr-DAPhen, to make a comprehensive comparison. The complexation behaviors of trivalent lanthanides and actinides with these three ligands were thoroughly studied using ^1H NMR titration, spectrophotometric titration, X-ray crystallography methods, and solvent extraction.

■ EXPERIMENTAL SECTION

Chemicals and Reagents. The lanthanide nitrates [$Ln(NO_3)_3\cdot 6H_2O$, where Ln(III) = La(III), Nd(III), Eu(III), Er(III), and Lu(III)], tetraethylammonium nitrate (Et_4NNO_3), methanol (CH_3OH), 3-nitrobenzotrifluoride, sulfoxide chloride, ultradry dichloromethane (DCM), and other reagents were of analytical grade or higher purity. 1,10-Phenanthroline-2,9-dicarboxylic acid, 2,2-bipyridine-6,6-dicarboxylic acid, pyridine-2,6-dicarboxylic acid chloride, and pyrrolidine were purchased and used directly without further purification. Stock solutions of the ^{241}Am and ^{152}Eu tracers in 0.5−4.0 M HNO_3 media were provided by China Institute of Atomic Energy.

Syntheses. The ligands used in this work were synthesized according to Figure 1, and the detailed synthesis procedures are presented in the following sections, and the characterizations are provided in Figures S1−S3.

Pyr-DAPhen. 1,10-Phenanthroline-2,9-dicarboxylic acid (1.50 g, 5.58 mmol) was dissolved in sulfoxide chloride (30.0 mL), and the resulting mixture was heated to reflux for 3 h under an argon atmosphere. After cooling to room temperature, sulfoxide chloride was removed by vacuum distillation, and a light-green solid product was obtained. Then excess pyrrolidine (4.0 g, 55.8 mmol) and 45.0 mL of ultradry DCM were added to the light-green solid at 0 °C, and the resulting mixture was stirred at room temperature for 36 h. After washing with a saturated sodium bicarbonate solution (120 mL) and extraction using chloroform several times, the combined organic extracts were dried with anhydrous sodium sulfate and evaporated under reduced pressure to obtain the crude product as a pale-yellow solid. After purification by column chromatography using DCM/CH_3OH (40:1, v/v) as the eluant and air drying, Pyr-DAPhen was obtained as a light-yellow solid (1.53 g) with a yield of 73%.

Pyr-BPyDA. 2,2-Bipyridine-6,6-dicarboxylic acid (1.00 g, 4.10 mmol) was reacted with sulfoxide chloride (30 mL) as described above. The resulting product was then reacted with excess pyrrolidine (2.91 g, 40.9 mmol) in ultradry DCM (35.0 mL) at room temperature for 36 h. The mixture was washed with a saturated sodium bicarbonate solution (120 mL) several times and then dried with anhydrous sodium sulfate. After DCM was distilled off, the residue was washed with ether several times and dried in a vacuum box at 60 °C to obtain Pyr-BPyDA as a pale-yellow solid (1.1 g) with a yield of 79%.

Pyr-PyDA. Excess pyrrolidine (3.48 g, 49.0 mmol) was reacted with pyridine-2,6-dicarboxylic acid chloride (1.00 g, 4.90 mmol) in ultradry DCM (35.0 mL) as described above. The residue, afforded from evaporation of the solvent, was washed with ether several times and dried in a vacuum box at 60 °C to obtain Pyr-PyDA as a light-yellow solid (1.0 g) with a yield of 76%.

NMR Titration. For the NMR titration experiments, the stock solutions of Pyr-DAPhen (15 mM), Pyr-BPyDA (15 mM), Pyr-PyDA (15 mM), $La(NO_3)_3$ (15 mM), and $Lu(NO_3)_3$ (15 mM) were all obtained by dissolving the weighed ligands $La(NO_3)_3{\cdot}6H_2O$ and $Lu(NO_3)_3{\cdot}6H_2O$ in CD_3OD, respectively. According to the certain molar ratios designed between the metal ions and ligands, certain volumes of lanthanides and ligand solutions were added to the NMR tubes to obtain a series of mixtures of La(III) or Lu(III) and ligands, with molar ratios increasing from 0 to 3.0. After the complexation equilibrium was reached, the ^1H NMR spectra were recorded on a Bruker AVANCE III model 500 MHz instrument.

UV−Vis Titration. UV−vis spectroscopic titrations were performed at 298 ± 1 K in CH_3OH on a Hitachi UH-5300 spectrophotometer (Japan). Et_4NNO_3 (10 or 50 mM) was used to control the ionic strength. For Pyr-BPyDA and Pyr-DAPhen, an appropriate volume of a $Ln(NO_3)_3$ (Ln = Nd, Eu) solution in CH_3OH was added to 2.2 mL of a ligand solution, and the concentration of the ligand was set as 0.02 mM. For Pyr-PyDA, to obtain the more accurate stability constants of 1:1 and 2:1 ligand-to-metal complexes formed with lanthanides, 2.0 mL of a $Nd(NO_3)_3$ (around 5.0 mM) solution was titrated by an appropriate volume of Pyr-PyDA (50 mM) dissolved in a CH_3OH solution. Notably, the concentrations of lanthanides used for the titrations were accurately determined by inductively coupled plasma optical emission spectrometry (730-ES, Varian Inc., America). After each addition of a lanthanide or ligand solution, the mixture was stirred in a quartz cell for 3 min to reach the complexation equilibrium, and then the absorption spectra were collected. The titration was stopped until no obvious changes were found in the absorption bands. The stability constants of Nd(III) and Eu(III) complexation with three ligands in CH_3OH were determined by the nonlinear-fitting method using the UV−vis spectrophotometric titration data with the *HypSpec* program.[41,53−56]

Single-Crystal X-ray Diffraction Measurements. Single crystals of the Pyr-PyDA, Pyr-BPyDA, and Pyr-DAPhen complexes with $Nd(NO_3)_3$, $Er(NO_3)_3$, and $La(NO_3)_3$ suitable for X-ray diffraction measurement were obtained by a solvent diffusion method. Pyr-BPyDA and Pyr-DAPhen and their corresponding lanthanide metal salts were dissolved in mixed solvents of CH_3OH and DCM with a molar ratio of 1:1 between the metal and ligand, and then the mixture solution was sealed in an atmosphere of diethyl ether. Pyr-PyDA and its corresponding lanthanide metal salts were dissolved in CH_3OH with an atmosphere of diethyl ether. After 2 days, single crystals of complexes of $Nd(Pyr\text{-}PyDA)(NO_3)_3{\cdot}CH_3OH$, $Nd(Pyr\text{-}BPyDA)(NO_3)_3$, $Er(Pyr\text{-}DAPhen)(NO_3)_3$, and $La(Pyr\text{-}DAPhen)(NO_3)_3{\cdot}CH_3OH$ were obtained. The single-crystal X-ray diffraction data were collected on Mo Kα radiation (tube operating at 50 kV and 1.4 mA) with a Bruker D8 Venture diffractometer. Detailed information on the bond lengths and angles is listed in Tables S1−S8.

Solvent Extraction. The aqueous phase for the extraction was spiked with trace amounts of $^{241}Am(III)$ and $^{152,154}Eu(III)$ in a HNO_3 solution ranging from 0.5 to 4.0 M. The organic phases were obtained by directly dissolving the appropriate amounts of the three ligands in 3-nitrobenzotrifluoride (10 mM), respectively. Equal volumes of the organic and aqueous phases (0.5 mL) were vigorously shaken in a centrifuge tube for 3 h at 298 ± 1 K to reach the extraction equilibrium. ***Caution!*** *^{241}Am salts are seriously chemotoxic and strongly radioactive, so it could pose serious health threats! All radioactive experiments must be carried out in radiological facilities.* After phase separation by centrifugation, the concentrations of $^{241}Am(III)$ and $^{152,154}Eu(III)$ in aqueous phases before and after extraction were measured using a liquid scintillation spectrometer (Quantulus 1220 Ultra Model Scintillation spectrometer) to obtain the extraction distribution ratio (D), which is defined as the ratio of the concentrations (radioactivity counts) of $^{241}Am(III)$ and $^{152,154}Eu(III)$ between the organic and aqueous phases. $SF_{Am/Eu}$ was determined by the ratio D of $^{241}Am(III)$ to $^{152,154}Eu(III)$.[57]

RESULTS AND DISCUSSION

NMR Titration Studies. NMR titration is a simple but very effective method to explore the complex species formed between the organic ligands and diamagnetic metal ions in solution.[58−61] Because of the paramagnetic nature of Eu(III), in this work, diamagnetic La(III) or Lu(III) was used to identify the complex speciation formed between trivalent lanthanides and three ligands in nitrate media by ^1H NMR spectra in CD_3OD.

As shown in Figure 2a, two groups of well-defined peaks located at 8.06 and 7.83 ppm that appeared in the initial ^1H NMR spectrum (M/L = 0.0) correspond to the protons of H_1 and H_2 contained in the free Pyr-PyDA ligand. With increasing concentration of $La(NO_3)_3$, these two peaks showed an obvious downfield shift as the M/L ratio increased from 0.00 to 0.50, indicating the occurrence of a coordination reaction between the lanthanide ion and ligand. When the M/L ratios were varied from 0.50 to 1.00 with the presence of excess ligand in the solution, the two above-mentioned NMR peaks were greatly broadened, suggesting that 1:2 complex species might be formed. What is more, these two peaks became gradually distinguishable again when the M/L ratio was above 1.00, and upon further addition of the lanthanide solution, the patterns of these two peaks became constant. These results implied that the 1:1 La(III)/Pyr-PyDA complex was formed when excess La(III) was added. The formation of two complex species was also found in the NMR titration of Pyr-PyDA with $Lu(NO_3)_3$, as shown in Figure S4. Two peaks located at 8.06 and 7.83 ppm gradually disappeared, and four new groups of peaks at 8.44, 8.20, 8.11, and 7.96 ppm (1:1 complex species) became apparent as the M/L ratio was at 0.00−0.40. When the M/L ratio was above 0.80, the patterns of the peaks at 8.50 ppm became constant, suggesting that the 1:1 complex species formed. In summary, both 1:1 and 1:2 complex species can be formed between lanthanides and Pyr-PyDA.

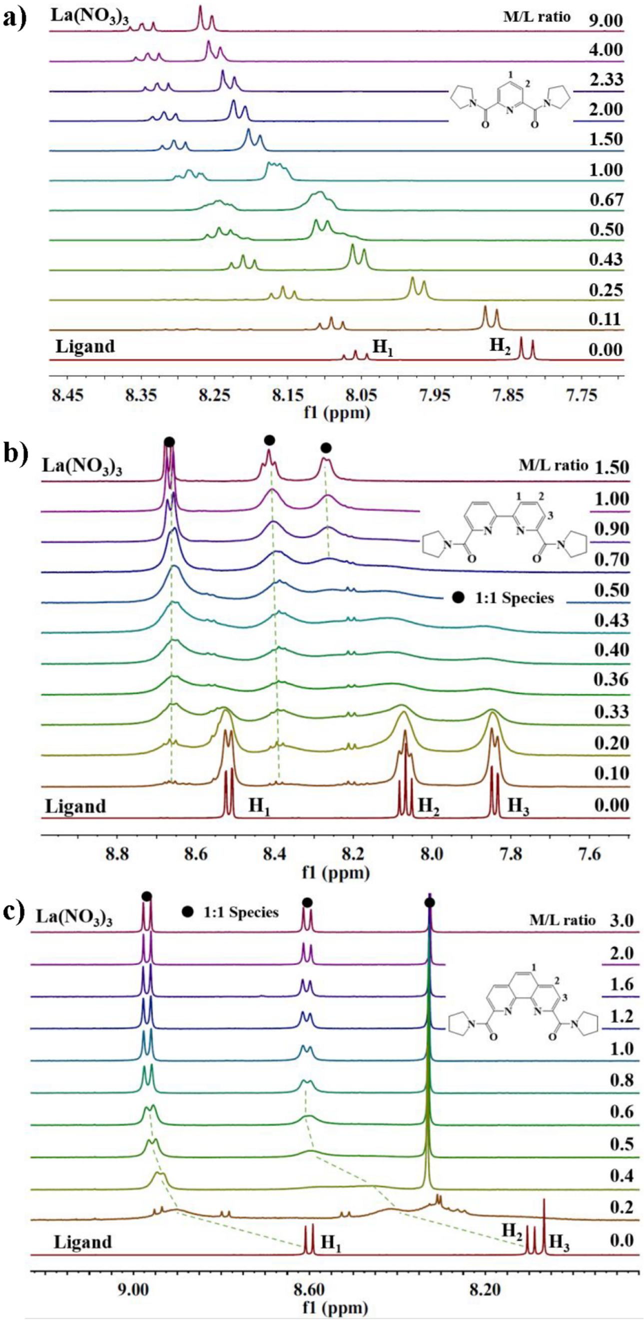

Figure 2. ^{1}H NMR titration spectra of (a) Pyr-PyDA (15.0 mM), (b) Pyr-BPyDA (15.0 mM), and (c) Pyr-DAPhen (15.0 mM) titrated with La$(NO_3)_3$ in CD_3OD. (M/L denotes the metal/ligand molar ratio.)

However, quite different from that of Pyr-PyDA, the complexation behaviors were clearly obtained from the ^{1}H NMR titrations of Pyr-BPyDA and Pyr-DAPhen with La$(NO_3)_3$ in CD_3OD. As presented in Figure 2b, at the beginning, the three NMR peaks related to the protons of H_1, H_2, and H_3 of the free Pyr-BPyDA ligand located at 8.51, 8.07, and 7.85 ppm were greatly broadened upon the addition of a La$(NO_3)_3$ solution, suggesting the formation of new complex species in the titrated mixture. Meanwhile, the titration results implied that only the 1:1 La(III)/Pyr-BPyDA complex was formed because three broadened peaks (8.67, 8.40, and 8.27 ppm) became gradually clear when the M/L ratio was above 0.10, and upon the further addition of a lanthanide solution, there were no new NMR signals until the M/L ratio reached 1.50. For Pyr-DAPhen titrated with La$(NO_3)_3$ (Figure 2c), the changing trend in the spectra was more clear than that of Pyr-BPyDA. The original ^{1}H NMR signals of Pyr-DAPhen located at 8.60, 8.10, and 8.07 ppm scribbled to the protons of H_1, H_2, and H_3 in the 1,10-phenanthroline framework of the ligand were all shifted downfield and were significantly broadened upon the addition of La$(NO_3)_3$ when the M/L ratio was below 1.0. The results of the ^{1}H NMR titration indicated that the 1:1 metal/ligand complex was formed in a solution as the transformation to a new complex species and finished after the addition of 1.0 equiv of lanthanide nitrate into a ligand solution. The formation of similar 1:1 metal/ligand complexes was also reported in other 1,10-phenanthroline ligand complexation with Ln$(NO_3)_3$ in CH_3OH.[16,21] It can be concluded that the tetradentate Pyr-BPyDA and Pyr-DAPhen mainly formed the 1:1 ligand/metal complex with lanthanide ions in solution, but the tridentate ligand Pyr-PyDA could form both 1:1 and 1:2 complex species, which is also verified by the UV−vis titration and single-crystal X-ray diffraction studies as discussed below.

UV−Vis Titration Analysis. The stability constants of the typical lanthanide complexes formed with three ligands were further determined by UV−vis titration under ionic strengths of 0.01 or 0.05 M Et_4NNO_3 in a CH_3OH solution at 298 K. The spectrophotometric titration spectra and fitted molar absorptivities of Nd(III) complexes formed with three ligands are shown in Figure 3. The titration spectra of the 1:1 (or 1:2)-type Nd(III) complexes with three ligands exhibited significantly different trends.

As can be seen from Figure 3a, with increasing concentration of Pyr-PyDA, the initial absorption band of Nd(III) in the range of 570−590 nm gradually increased and slightly red-shifted. At the last titration stage, two new absorption peaks centered at 574 and 592 nm were observed, indicating the formation of new complex species in solution. Upon further analysis with the *HypSpec* program, it was found that the spectral changes in the titration data could be best fitted by the successive formation of two Nd(III) complexes. However, for Pyr-BPyDA, the changes in the absorption spectra were quite different (Figure 3b); upon the addition of a Nd(III) solution, the absorption peak of Pyr-BPyDA at 286 nm gradually decreased, while one new absorption band at around 320 nm increased. Therefore, two obvious isosbestic points located at 267 and 298 nm were formed, suggesting that one single Nd(III)/Pyr-BPyDA complex might be formed in solution. Similar trends were also found in the titration spectra of Pyr-DAPhen with Nd(III) at the same conditions. As shown in Figure 3c, with increasing concentration of Nd(III), the absorption bands varying from 257 to 283 nm gradually decreased and the two absorption bands centered at 250 and 296 nm increased, which resulted in the formation of two isosbestic points located at 257 and 283 nm, respectively. These results indicated that Pyr-DAPhen formed one single complex species with Nd(III) in CH_3OH. Further, these spectral changes of Pyr-BPyDA and Pyr-DAPhen titrated with neodymium(III) nitrate could be well fitted by a one-to-one complex formation reaction, based on the *HypSpec*[53,54] program.

Similar results were also obtained from the titration data of Pyr-BPyDA and Pyr-DAPhen complexation with Eu(III) under identical experimental conditions (Figures S5b,c). However,

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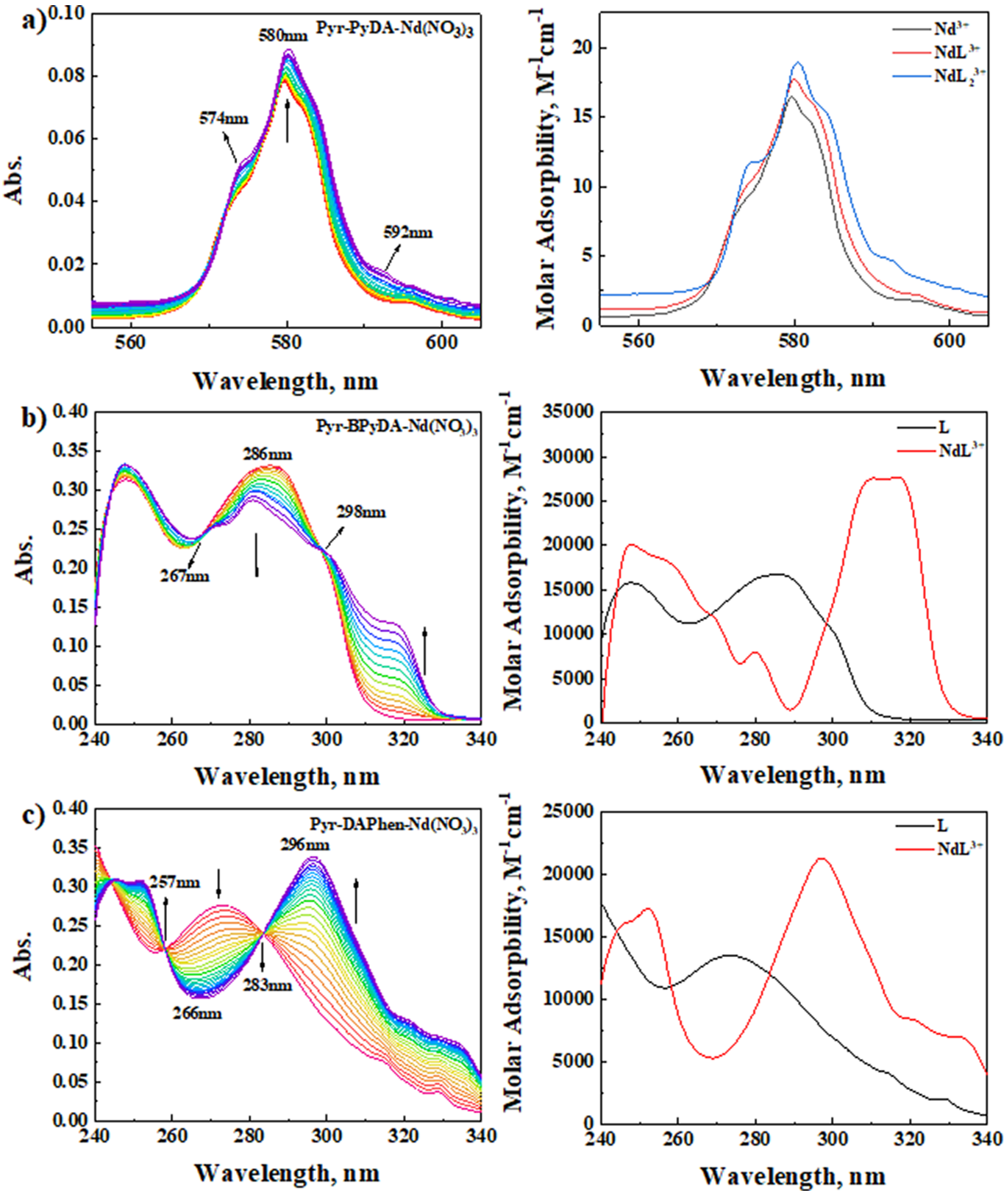

Figure 3. Spectrophotometric titrations of the three ligands (a) Pyr-PyDA, (b) Pyr-BPyDA, and (c) Pyr-DAPhen complexed with $Nd(NO_3)_3$ in a CH_3OH solution (T = 298 K). Left: Normalized titration spectra collected. Right: Calculated molar absorptivities of Nd(III) complexes with the three ligands. (a) $C_{Nd(III)}/C_L$ = 4.60 mM/50 mM, V_0 = 2.00 mL, a total of 0.78 mL titrant was added, and I = 0.05 M Et_4NNO_3. (b) $C_L/C_{Nd(III)}$ = 0.02 mM/0.45 mM, V_0 = 2.20 mL, a total of 0.21 mL titrant was added, and I = 0.01 M Et_4NNO_3. (c) $C_L/C_{Nd(III)}$ = 0.02 mM/0.45 mM, V_0 = 2.20 mL, a total of 0.12 mL titrant was added, and I = 0.01 M Et_4NNO_3.

for tridentate Pyr-PyDA (Figure S5a) from the absorption data of ligands titrated with Eu(III), we cannot obtain the stability constants of 1:1 and 1:2 species, which was different from the titration of Nd(III) with the ligand (Figure 3a). The minor difference between the absorption spectra of the 1:1 and 1:2 metal-to-ligand complexes as well as the relative weak complexation ability of Pyr-PyDA might result in this lack of success. For comparison, we only presented the stability constant of the 1:1 Eu(III)/Pyr-PyDA complex by ignoring the minor ratio of the 1:2 complex species formed in solution. The calculated stability constants of Eu(III) and Nd(III) complexes with three ligands were summarized in Table 1.

The stability constant (log β) of the 1:1 Eu(III) complex with Pyr-DAPhen was determined to be 5.46 ± 0.04, which was approximately 1−2 orders of magnitude larger than those of Pyr-BPyDA (4.14 ± 0.01) and Pyr-PyDA (2.73 ± 0.01), respectively. This trend of the complexing abilities of the three ligands toward trivalent lanthanides was also confirmed by the Nd(III) titration studies (Table 1). These results preliminarily indicated that the highly preorganized phenanthroline-derived ligands with strong rigidity held much stronger affinity for trivalent lanthanides than those bipyridine- or pyridine-derived amide-type ligands. This conclusion has also been previously proved by theoretical calculations for three structurally similar ligands (Et-Tol-DAPhen, Et-Tol-BPyDA, and Et-Tol-PyDA)

Table 1. Stability Constants (log β) of the Complexation Reactions of Ln(III) with the Three Ligands Obtained by the Spectrophotometry Method in CH_3OH at 298 K

metal ion	ligand	reaction	log β	ionic medium
Eu^{3+}	Pyr-PyDA	$L + Eu^{3+} \rightleftharpoons EuL^{3+}$	2.73 ± 0.01	0.01 M Et_4NNO_3
	Pyr-BPyDA	$L + Eu^{3+} \rightleftharpoons EuL^{3+}$	4.14 ± 0.01	0.01 M Et_4NNO_3
	Pyr-DAPhen	$L + Eu^{3+} \rightleftharpoons EuL^{3+}$	5.46 ± 0.04	0.01 M Et_4NNO_3
Nd^{3+}	Pyr-PyDA	$L + Nd^{3+} \rightleftharpoons NdL^{3+}$	2.95 ± 0.13	0.05 M Et_4NNO_3
	Pyr-PyDA	$2L + Nd^{3+} \rightleftharpoons NdL_2^{3+}$	5.03 ± 0.10	0.05 M Et_4NNO_3
	Pyr-BPyDA	$L + Nd^{3+} \rightleftharpoons NdL^{3+}$	4.21 ± 0.03	0.01 M Et_4NNO_3
	Pyr-DAPhen	$L + Nd^{3+} \rightleftharpoons NdL^{3+}$	5.47 ± 0.03	0.01 M Et_4NNO_3

complexed with trivalent Am(III) and Eu(III) using DFT methods.[52] In addition, a clear trend for the complexation ability of these three ligands was found between Nd(III) and Eu(III). As listed in Table 1, for a given ligand, the stability constant of Nd(III) (1:1 complex) was always slightly larger than that of Eu(III) under identical conditions. Similar results were also found in the complexation of lanthanides with a phenanthroline-derived phosphonate ligand, C4-POPhen.[57] The stability constant of 1:1 Eu(III)/C4-POPhen was 5.03 ± 0.03, which was smaller than that of Nd(III) (5.43 ± 0.02). This might have resulted from the better size match of the coordination cavity built by a given ligand for Nd(III) than Eu(III). These stability constant studies clearly showed that the complexation ability of the three ligands toward lanthanides decreases in the order of Pyr-DAPhen > Pyr-BPyDA > Pyr-PyDA, indicating that the central N-heterocyclic core of these N,O-mixed amide-type ligands had a significant effect on their complexation ability with f-block elements.

Crystal Structures of Lanthanide Complexes. In order to provide more microscopic information for elucidating the complexation mechanisms of these three ligands with trivalent lanthanides and actinides, single crystals of the Pyr-PyDA, Pyr-BPyDA, and Pyr-DAPhen complexes with trivalent lanthanides suitable for X-ray diffraction analysis were prepared using the solvent diffusion method.[62,63] The crystal structures of the typical lanthanide complexes with three ligands, $Nd(Pyr\text{-}PyDA)(NO_3)_3CH_3OH$ (**1**), $Nd(Pyr\text{-}BPyDA)(NO_3)_3$ (**2**), $Er(Pyr\text{-}DAPhen)(NO_3)_3$ (**3**), and $La(Pyr\text{-}DAPhen)(NO_3)_3CH_3OH$ (**4**), are presented in Figures 4 and 5, and the selected average bond distances of these crystal structures were comparatively listed in Table 2. The detailed structural refinement parameters are given Table 3. Other information of the bond length and bond angle data are given in the Supporting Information.

The complexes of **1** and **2** are crystallized in the triclinic space group $P\bar{1}$ and monoclinic space group $P2_1/c$, respectively. As displayed in Figure 4a,b, in complex **1**, Nd(III) is 10-coordinated with a tridentate Pyr-PyDA molecule and three bidentate nitrate ions as well as one additional CH_3OH molecule. The average bond distance of N_L−Nd is 2.63(14) Å, which is slightly longer than the bond distance of O_L−Nd [2.46(13) Å]. The same observation can be found in other lanthanide complexes with N,O-mixed ligands because the basicity of the N donor is "softer" than that of the O donor.[29,64−66] Compared with another N-heterocyclic core ligand (EtBTP) with the Nd(III) complex $[Nd(EtBTP)_3][BPh_4]_3\cdot 3CH_3CN$[67] with 9-coordination, the N_L−Nd distance in complex **1** is slightly longer than that in $[Nd(EtBTP)_3][BPh_4]_3\cdot 3CH_3CN$ (2.57 Å). For complex **2** (Figure 4c,d), the Nd(III) complex is 10-coordinated with one tetradentate Pyr-BPyDA molecule and three bidentate nitrate

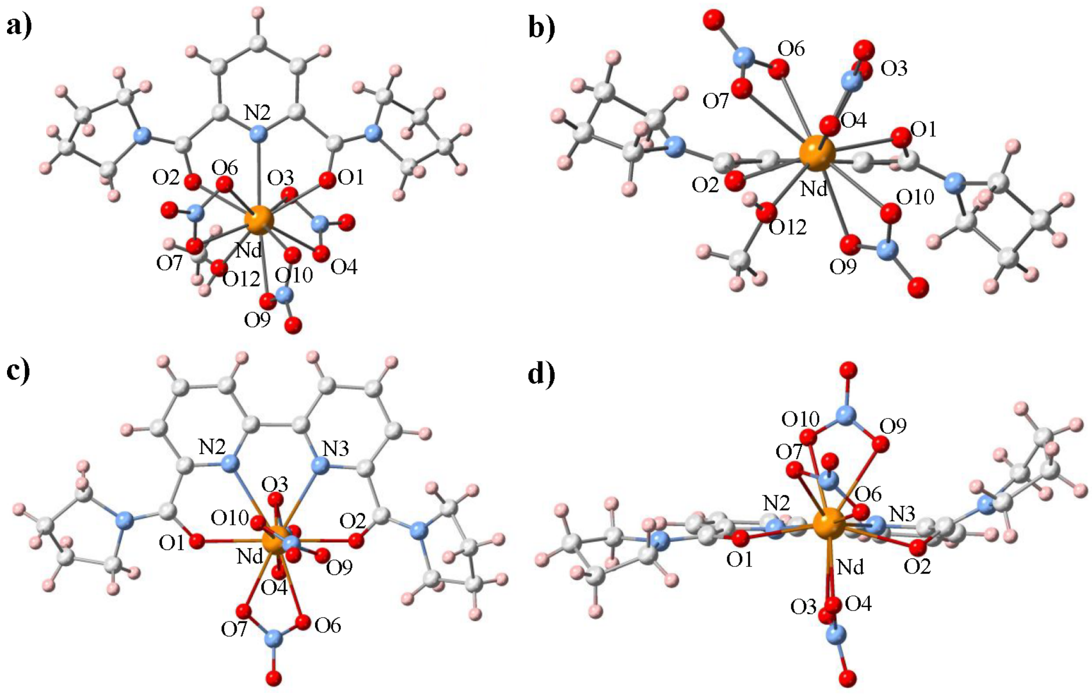

Figure 4. Crystal structure of **1**: (a) top view; (b) side view. Crystal structure of **2**: (c) top view; (d) side view. Orange, red, blue, white, and pink colors represent the Nd, O, N, C, and H atoms, respectively.

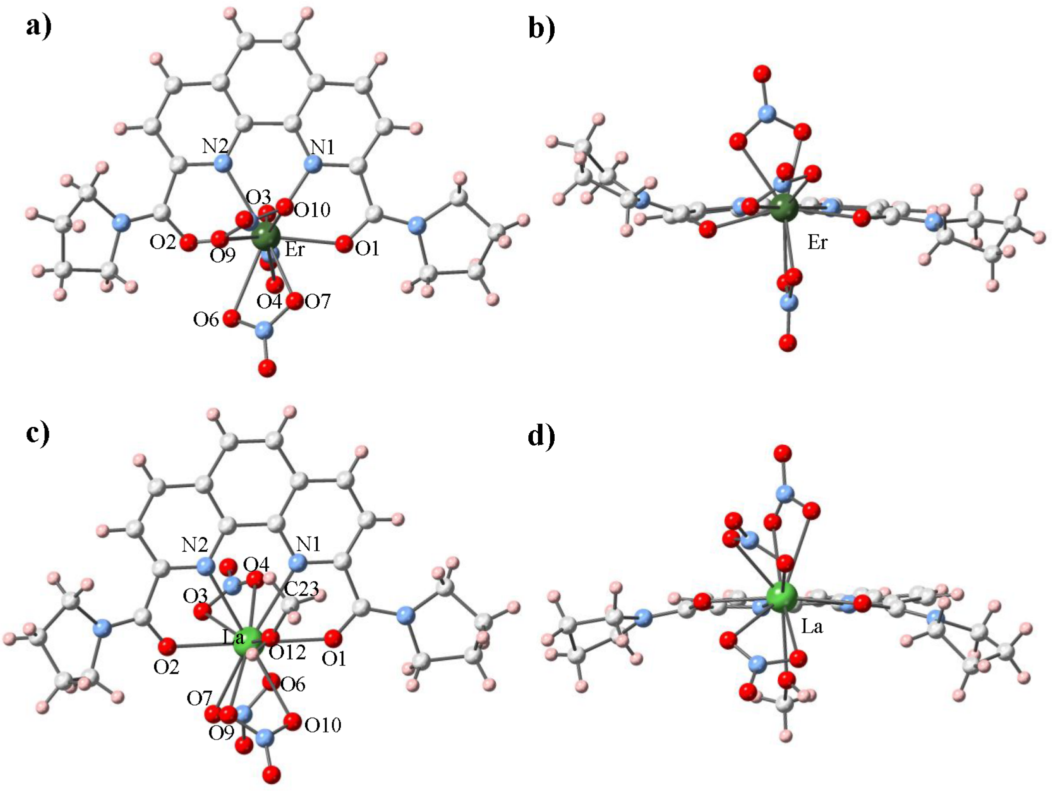

Figure 5. Crystal structure of **3**: (a) top view; (b) side view. Crystal structure of **4**: (c) top view; (d) side view. Dark-green, light-green, red, blue, white, and pink colors represent the Er, La, O, N, C, and H atoms, respectively.

Table 2. Average Bond Distances (Å) of 1−4 from the Crystal Data

complex	metal ionic radius	M−N$_L$	M−O$_L$	M−O$_N$
1	0.98	2.63(14)	2.46(13)	2.58(14)
2	0.98	2.63(12)	2.43(10)	2.55(11)
3	0.89	2.54(16)	2.36(14)	2.46(15)
4	1.03	2.77(17)	2.50(15)	2.66(16)

ions without a solvent molecule. The mean bond length from the central metal to the N atoms of the bipyridine ring is 2.63(12) Å, and that from the central metal to the O atoms of two amide groups is 2.43(10) Å. This Nd−N bond distance is almost the same as that in complex **1**, but the average Nd−O bond length [2.43(10) Å] is slightly shorter than that in complex **1**, suggesting that the stronger affinity of Pyr-BPyDA than Pyr-PyDA toward lanthanides probably resulted from the stronger Nd−O bonding.

Figure 5 shows the crystal structures of the 1:1 La(III) and Er(III) complexes with Pyr-DAPhen, which are crystallized as the monoclinic space groups $C2/c$ and $P2_1/n$, respectively. Similar to complex **2**, the central metal Er(III) in the Er(Pyr-DAPhen)(NO$_3$)$_3$ complex is also 10-coordinated with one tetradentate Pyr-BPyDA molecule and three bidentate nitrate ions. Similar structures of the lanthanide complexes have also been reported in other tetradentate ligands like DAPhen and CyMe$_4$-BTBP complexed with lanthanides in the solid state.[57] The mean bond distance from the central metal to the phenanthroline N atoms is 2.54(16) Å, and that from the central metal to the O atoms of the amide groups is 2.36(14) Å. However, different from this 10-fold coordination of Er(III) in complex **3**, La(III) in complex **4** is 11-coordinated with one Pyr-DAPhen molecule and three bidentate nitrate ions as well as one extra CH$_3$OH molecule. The larger radius of La(III) (1.03 Å) than Er(III) (0.89 Å)[29] might lead to its larger coordination number. What is more, the average bond distance of La−N$_L$ is 2.77(17) Å, which is obviously longer than that of Er−N$_L$ in complex **3**. Additionally, the central metal La(III) in complex **4** is nearly located in the phenanthroline plane with a O1−La−O2 bond angle of 172.27(6)°. Two pyrrole groups are almost on the same side of the phenanthroline plane. Compared to complex **4**, the position of the central metal and the orientation of two pyrrole groups in complex **3** are changed. As presented in Figure 5b, the central metal Er(III) is distorted away from the phenanthroline plane with a O1−Er−O2 angle of 155.56(5)°, and meanwhile two pyrrole moieties are located on the two sides of the phenanthroline plane. The smaller ionic radius of Er(III) than La(III) resulting from lanthanide contraction makes the coordination space too crowded to accommodate two pyrrole moieties on the same side. This conformation can reduce the thermodynamic energy to stabilize the complex in the solid state.[21]

As listed in Table 2, all of the key M−N and M−O bond distances in these four lanthanide complexes decreased as the lanthanide series traversed from light to heavy lanthanide elements, as expected because of lanthanide contraction. Also, the average Nd/Er/La−O$_L$ bond length [2.46(13)/2.43(10)/2.36(14)/2.50(15) Å] is shorter than that of Nd/Er/La−N$_L$ [2.63(14)/2.63(12)/2.54(16)/2.77(17) Å] because the basicity of the O donor is harder than that of the soft N donor. Similar results have also been found in the lanthanide complexes with other N,O-mixed ligands.[3]

Solvent Extraction Properties. Solvent extraction experiments were performed to evaluate the ability of the three

Table 3. Crystal Data and Structure Refinement for 1−4

	1	2	3	4
CCDC	2060543	2060538	2060541	2060542
empirical formula	$C_{16}H_{23}N_6NdO_{12}$	$C_{20}H_{22}N_7NdO_{11}$	$C_{22}H_{22}ErN_7O_{11}$	$C_{23}H_{26}LaN_7O_{12}$
fw	635.64	680.68	727.72	731.42
temperature/K	170	170	170	170
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$C2/c$
a/Å	9.578(3)	19.4601(5)	8.4652(2)	24.6729(5)
b/Å	10.172(3)	8.4589(2)	19.4863(5)	17.6631(3)
c/Å	13.823(4)	16.2482(4)	16.0858(4)	16.1057(4)
α/deg	98.304(13)	90	90	90
β/deg	97.412(12)	112.8710(10)	105.2220(10)	128.5970(10)
γ/deg	115.545(11)	90	90	90
volume/$Å^3$	1174.5(6)	2464.36(11)	2560.35(11)	5485.6(2)
Z	2	4	4	8
ρ_{calc}/ g cm^{-3}	1.797	1.835	1.888	1.771
μ/mm^{-1}	2.283	2.181	3.353	1.635
F(000)	634	1356	1436	2928
cryst size/mm^3	0.32 × 0.19 × 0.16	0.16 × 0.12 × 0.08	0.1 × 0.05 × 0.04	0.08 × 0.05 × 0.04
radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ range for data collection/deg	4.554−54.18	5.016−72.676	4.988−72.454	4.612−68.696
index ranges	$-10 \le h \le 12$, $-13 \le k \le 12$, $-17 \le l \le 17$	$-32 \le h \le 32$, $-14 \le k \le 10$, $-27 \le l \le 24$	$-13 \le h \le 11$, $-32 \le k \le 31$, $-22 \le l \le 26$	$-36 \le h \le 39$, $-26 \le k \le 27$, $-24 \le l \le 25$
reflns colld	28511	65675	67789	33814
indep reflns	5153 [R_{int} = 0.0246; R_σ = 0.0182]	11900 [R_{int} = 0.0379; R_σ = 0.0296]	10868 [R_{int} = 0.0476; R_{sigma} = 0.0390]	11398 [R_{int} = 0.0368; R_σ = 0.0491]
data/restraints/param	5153/3/320	11900/0/352	10868/0/370	11398/102/429
GOF on F^2	1.059	1.077	1.042	1.02
final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0139, wR_2 = 0.0351	R_1 = 0.0244, wR_2 = 0.0494	R_1 = 0.0294, wR_2 = 0.0465	R_1 = 0.0357, wR_2 = 0.0615
final R indexes (all data)	R_1 = 0.0142, wR_2 = 0.0353	R_1 = 0.0320, wR_2 = 0.0527	R_1 = 0.0473, wR_2 = 0.0518	R_1 = 0.0580, wR_2 = 0.0701
largest diff peak/hole/ e $Å^{-3}$	0.39/−0.51	0.81/−0.87	0.79/−1.02	0.67/−0.77

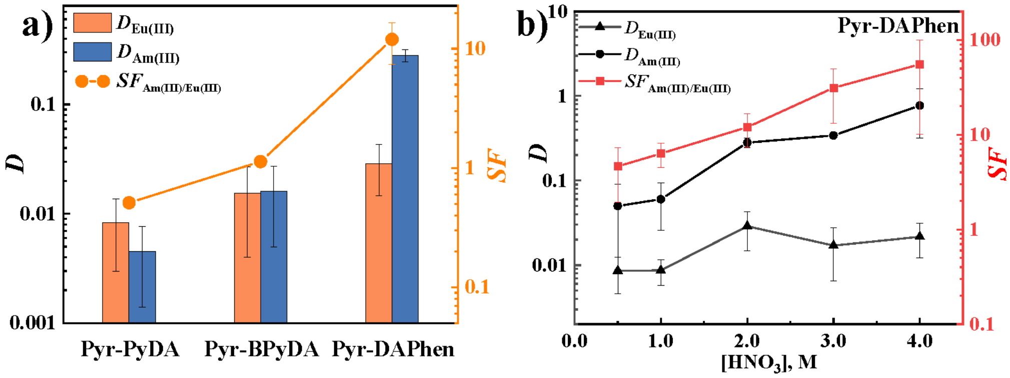

Figure 6. (a) Comparison of the extraction ability of Am(III) and Eu(III) by the three ligands in a 2.0 M HNO_3 solution. (b) Extraction of Am(III) and Eu(III) by Pyr-DAPhen in 3-nitrobenzotrifluoride as a function of the HNO_3 concentration (mixing time = 3 h; temperature = 298 ± 1 K).

ligands to selectively extract An(III) over Ln(III). The ^{241}Am(III) and ^{152,154}Eu(III) radiotracers were used as representative ions of trivalent actinide and lanthanide ions, respectively. From Figure 6a, we can see that Pyr-DAPhen exhibited the highest distribution ratios (D) for Am(III) and Eu(III) among the three ligands tested, despite the relatively very weak extraction ability of these ligands toward Am(III) and Eu(III). The $SF_{Am(III)/Eu(III)}$ value of Pyr-DAPhen was much higher than those of Pyr-PyDA and Pyr-BPyDA at 2.0 M HNO_3 (the $SF_{Am(III)/Eu(III)}$ value of Pyr-DAPhen was about 12.0, but for Pyr-PyDA and Pyr-BPyDA, it was 0.5 and 1.1, respectively). Besides, with increasing concentration of HNO_3 from 0.5 to 4.0 M (Figure 6b), the distribution ratio values of Pyr-DAPhen for Am(III) increased from 0.05 to 0.8. Meanwhile, the resulting $SF_{Am(III)/Eu(III)}$ values increased significantly with increasing HNO_3 concentration, and $SF_{Am(III)/Eu(III)}$ was up to 55 at 4.0 M HNO_3. These results demonstrate that the preorganized cis-locked phenanthroline-derived Pyr-DAPhen held a stronger extraction ability and a higher extraction selectivity toward trivalent actinides over lanthanides than its structurally similar bipyridine- or pyridine-based ligands in highly acidic solutions. These findings also agree well with the results of the UV−vis titration and single-crystal structural studies of the lanthanide complexes.

■ CONCLUSIONS

Three N,O-hybrid diamide ligands with different N-heterocyclic cores (phenanthroline, bipyridine, and pyridine) were synthesized, and their complexation as well as extraction mechanisms with trivalent lanthanides and actinides was systematically studied. The formation of only a 1:1 metal/ligand complex between trivalent lanthanides with Pyr-BPyDA and Pyr-DAPhen in nitrate media was identified by ^{1}H NMR titration studies, while Pyr-PyDA could form both 1:1 and 1:2 complexes with lanthanides. The stability constants of these 1:1 complexes formed between three ligands with two typical lanthanides, Nd(III) and Eu(III), indicated that the complexation strength of the three ligands with lanthanides decreased in the order of Pyr-DAPhen > Pyr-BPyDA > Pyr-PyDA. Furthermore, the structures of the 1:1 lanthanide complexes with these three ligands were thoroughly elucidated by the single-crystal X-ray diffraction technique. It is found that the 1:1 Nd(III) and Er(III) complexes with Pyr-PyDA, Pyr-BPyDA, and Pyr-DAPhen were 10-coordinated, while the 1:1 La(III) complex with Pyr-DAPhen was 11-coordinated with one ligand molecule and three nitrate ions as well as one extra CH_3OH molecule. The solvent extraction studies demonstrate that the preorganized ligand Pyr-DAPhen with a rigid 1,10-phenanthroline core held the strongest affinity and highest extraction selectivity for trivalent actinides over lanthanides among the three ligands. The results from this work help us to better understand the influence of a N-heterocyclic core on the binding capability of diamide ligands toward trivalent lanthanides and actinides and design more efficient extractants for the separation of MAs from highly active nuclear waste.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00715.

> ^{1}H NMR spectra of ligands, ^{1}H NMR titration spectra, spectrophotometric titration spectra, and bond distances and angles for crystal structures of complexes (PDF)

Accession Codes

CCDC 2060538 and 2060541−2060543 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Lemport, P. S.; Matveev, P. I.; Yatsenko, A. V.; Evsiunina, M. V.; Petrov, V. S.; Tarasevich, B. N.; Roznyatovsky, V. A.; Dorovatovskii, P. V.; Khrustalev, V. N.; Zhokhov, S. S.; Solov'ev, V. P.; Aslanov, L. A.; Petrov, V. G.; Kalmykov, S. N.; Nenajdenko, V. G.; Ustyniuk, Y. A. The impact of alicyclic substituents on the extraction ability of new family of 1,10-phenanthroline-2,9-diamides. *RSC Adv.* **2020**, *10*, 26022−26033.

(2) Magill, J.; Berthou, Y. V.; Haas, Y. D.; Galy, Y. J.; Schenkel, Y. R.; Wiese, H. W.; Heusener, G.; Tommasi, Z. J.; Youinou, G. Impact limits of partitioning and transmutation scenarios on the radiotoxicity of actinides in radioactive waste. *J. Infect. Dis.* **2003**, *176*, 20−26.

(3) Chen, B.; Liu, J.; Lv, L.; Yang, L.; Luo, S.; Yang, Y.; Peng, S. Complexation of Lanthanides with N, N, N′, N′-Tetramethylamide Derivatives of Bipyridinedicarboxylic Acid and Phenanthrolinedicarboxylic Acid: Thermodynamics and Coordination Modes. *Inorg. Chem.* **2019**, *58*, 7416−7425.

(4) Scaravaggi, S.; Macerata, E.; Galletta, M.; Mossini, E.; Casnati, A.; Anselmi, M.; Sansone, F.; Mariani, M. Hydrophilic 1,10-phenanthroline derivatives for selective Am(III) stripping into aqueous solutions. *J. Radioanal. Nucl. Chem.* **2014**, *303*, 1811−1820.

(5) Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Drew, M. G.; Desreux, J. F.; Vidick, G.; Bouslimani, N.; Modolo, G.; Wilden, A.; Sypula, M.; Vu, T. H.; Simonin, J. P. Highly efficient separation of actinides from lanthanides by a phenanthroline-derived bis-triazine ligand. *J. Am. Chem. Soc.* **2011**, *133*, 13093−13102.

(6) Galletta, M.; Scaravaggi, S.; Macerata, E.; Famulari, A.; Mele, A.; Panzeri, W.; Sansone, F.; Casnati, A.; Mariani, M. 2,9-Dicarbonyl-1,10-phenanthroline derivatives with an unprecedented Am(III)/Eu(III) selectivity under highly acidic conditions. *Dalton Trans.* **2013**, *42*, 16930−16938.

(7) Veliscek-Carolan, J.; Rawal, A. Zirconium bistriazolylpyridine phosphonate materials for efficient, selective An(III)/Ln(III) separations. *Chem. Commun.* **2019**, *55*, 1168−1171.

(8) Salvatores, M. Nuclear fuel cycle strategies including Partitioning and Transmutation. *Nucl. Eng. Des.* **2005**, *235*, 805−816.

(9) Alyapyshev, M.; Babain, V.; Tkachenko, L.; Kenf, E.; Voronaev, I.; Dar'in, D.; Matveev, P.; Petrov, V.; Kalmykov, S.; Ustynyuk, Y. Extraction of actinides with heterocyclic dicarboxamides. *J. Radioanal. Nucl. Chem.* **2018**, *316*, 419−428.

(10) Salvatores, M.; Palmiotti, G. Radioactive waste partitioning and transmutation within advanced fuel cycles: Achievements and challenges. *Prog. Part. Nucl. Phys.* **2011**, *66*, 144−166.

(11) Gao, Y.; Parker, B. F.; Dau, P. V.; Dau, P. D.; Lohrey, T. D.; Gibson, J. K.; Arnold, J.; Teat, S. J.; Melchior, A.; Zhang, Z.; Rao, L. Coordination of 2,2′-(Trifluoroazanediyl)bis(N,N′-dimethylacetamide) with U(VI), Nd(III), and Np(V): A Thermodynamic and Structural Study. *Inorg. Chem.* **2019**, *58*, 15962−15970.

(12) Xu, C.; Tian, G.; Teat, S. J.; Rao, L. Complexation of U(VI) with dipicolinic acid: thermodynamics and coordination modes. *Inorg. Chem.* **2013**, *52*, 2750−2756.

(13) Simonnet, M.; Suzuki, S.; Miyazaki, Y.; Kobayashi, T.; Yokoyama, K.; Yaita, T. Lanthanide Intra-series Separation by a 1,10-Phenanthroline Derivative: Counterion Effect. *Solvent Extr. Ion Exch.* **2020**, *38*, 430−440.

(14) Liu, Y.; Yang, X.; Ding, S.; Wang, Z.; Zhang, L.; Song, L.; Chen, Z.; Wang, X. Highly Efficient Trivalent Americium/Europium Separation by Phenanthroline-Derived Bis(pyrazole) Ligands. *Inorg. Chem.* **2018**, *57*, 5782−5790.

(15) Manna, D.; Mula, S.; Bhattacharyya, A.; Chattopadhyay, S.; Ghanty, T. K. Actinide selectivity of 1,10-phenanthroline-2,9-dicarboxamide and its derivatives: a theoretical prediction followed by experimental validation. *Dalton Trans.* **2015**, *44*, 1332−1340.

(16) Xu, L.; Pu, N.; Li, Y.; Wei, P.; Sun, T.; Xiao, C. L.; Chen, J.; Xu, C. Selective Separation and Complexation of Trivalent Actinide and Lanthanide by a Tetradentate Soft-Hard Donor Ligand: Solvent Extraction, Spectroscopy, and DFT Calculations. *Inorg. Chem.* **2019**, *58*, 4420−4430.

(17) Bisson, J.; Dehaudt, J.; Charbonnel, M. C.; Guillaneux, D.; Miguirditchian, M.; Marie, C.; Boubals, N.; Dutech, G.; Pipelier, M.; Blot, V.; Dubreuil, D. 1,10-Phenanthroline and non-symmetrical 1,3,5-triazine dipicolinamide-based ligands for group actinide extraction. *Chem. - Eur. J.* **2014**, *20*, 7819−7829.

(18) Ustynyuk, Y. A.; Gloriozov, I. P.; Kalmykov, S. N.; Mitrofanov, A. A.; Babain, V. A.; Alyapyshev, M. Y.; Ustynyuk, N. A. Pyridinedicarboxylic Acid Diamides as Selective Ligands for Extraction and Separation of Trivalent Lanthanides and Actinides: DFT Study. *Solvent Extr. Ion Exch.* **2014**, *32*, 508−528.

(19) Ustynyuk, Y. A.; Borisova, N. E.; Babain, V. A.; Gloriozov, I. P.; Manuilov, A. Y.; Kalmykov, S. N.; Alyapyshev, M. Y.; Tkachenko, L. I.; Kenf, E. V.; Ustynyuk, N. A. N,N′-Dialkyl-N,N′-diaryl-1,10-phenanthroline-2,9-dicarboxamides as donor ligands for separation of rare earth elements with a high and unusual selectivity. DFT computational and experimental studies. *Chem. Commun.* **2015**, *51*, 7466−7469.

(20) Alyapyshev, M. Y.; Babain, V. A.; Ustynyuk, Y. A. Recovery of minor actinides from high-level wastes: modern trends. *Russ. Chem. Rev.* **2016**, *85*, 943−961.

(21) Xiao, C. L.; Wang, C. Z.; Yuan, L. Y.; Li, B.; He, H.; Wang, S.; Zhao, Y. L.; Chai, Z. F.; Shi, W. Q. Excellent selectivity for actinides with a tetradentate 2,9-diamide-1,10-phenanthroline ligand in highly acidic solution: a hard-soft donor combined strategy. *Inorg. Chem.* **2014**, *53*, 1712−1720.

(22) Xiao, C. L.; Wu, Q. Y.; Wang, C. Z.; Zhao, Y. L.; Chai, Z. F.; Shi, W. Q. Quantum chemistry study of uranium(VI), neptunium(V), and plutonium(IV,VI) complexes with preorganized tetradentate phenanthrolineamide ligands. *Inorg. Chem.* **2014**, *53*, 10846−53.

(23) Xiao, C. L.; Wang, C. Z.; Mei, L.; Zhang, X. R.; Wall, N.; Zhao, Y. L.; Chai, Z. F.; Shi, W. Q. Europium, uranyl, and thorium-phenanthroline amide complexes in acetonitrile solution: an ESI-MS and DFT combined investigation. *Dalton Trans.* **2015**, *44*, 14376−87.

(24) Harwood, L.; Lewis, F.; Hudson, M. Development of Highly Selective Ligands for Separations of Actinides from Lanthanides in the Nuclear Fuel Cycle. *Synlett* **2011**, *2011*, 2609−2632.

(25) Panak, P. J.; Geist, A. Complexation and extraction of trivalent actinides and lanthanides by triazinylpyridine N-donor ligands. *Chem. Rev.* **2013**, *113*, 1199−236.

(26) Leoncini, A.; Huskens, J.; Verboom, W. Ligands for f-element extraction used in the nuclear fuel cycle. *Chem. Soc. Rev.* **2017**, *46*, 7229−7273.

(27) Bessen, N. P.; Jackson, J. A.; Jensen, M. P.; Shafer, J. C. Sulfur donating extractants for the separation of trivalent actinides and lanthanides. *Coord. Chem. Rev.* **2020**, *421*, 213446.

(28) Geist, A.; Panak, P. J. Recent Progress in Trivalent Actinide and Lanthanide Solvent Extraction and Coordination Chemistry with Triazinylpyridine N Donor Ligands. *Solvent Extr. Ion Exch.* **2021**, *39*, 128−151.

(29) Alyapyshev, M.; Ashina, J.; Dar'in, D.; Kenf, E.; Kirsanov, D.; Tkachenko, L.; Legin, A.; Starova, G.; Babain, V. 1,10-Phenanthroline-2,9-dicarboxamides as ligands for separation and sensing of hazardous metals. *RSC Adv.* **2016**, *6*, 68642−68652.

(30) Wessling, P.; Trumm, M.; Macerata, E.; Ossola, A.; Mossini, E.; Gullo, M. C.; Arduini, A.; Casnati, A.; Mariani, M.; Adam, C.; Geist, A.; Panak, P. J. Activation of the Aromatic Core of 3,3′-(Pyridine-2,6-diylbis(1H-1,2,3-triazole-4,1-diyl))bis(propan-1-ol)-Effects on Extraction Performance, Stability Constants, and Basicity. *Inorg. Chem.* **2019**, *58*, 14642−14651.

(31) Merrill, D.; Hancock, R. D. Metal ion selectivities of the highly preorganized tetradentate ligand 1,10-phenanthroline-2,9-dicarboxamide with lanthanide(III) ions and some actinide ions. *Radiochim. Acta* **2011**, *99*, 161−166.

(32) Yang, X.; Xu, L.; Hao, Y.; Meng, R.; Zhang, X.; Lei, L.; Xiao, C. Effect of Counteranions on the Extraction and Complexation of Trivalent Lanthanides with Tetradentate Phenanthroline-Derived Phosphonate Ligands. *Inorg. Chem.* **2020**, *59*, 17453−17463.

(33) Kolarik, Z.; Mullich, U.; Gassner, F. Extraction of Am(III) and Eu(III) nitrates by 2−6-di-(5,6-dipropyl-1,2,4-triazin-3-yl)pyridines 1. *Solvent Extr. Ion Exch.* **1999**, *17*, 1155−1170.

(34) Case, F. H. The preparation of 2,4- and 2,6-bis-triazinyl and triazolinyl derivatives of pyridine. *J. Heterocycl. Chem.* **1971**, *8*, 1043−1046.

(35) Hudson, M. J.; Boucher, C. E.; Braekers, D.; Desreux, J. F.; Drew, M. G. B.; Foreman, M. R. S. J.; Harwood, L. M.; Hill, C. m.; Madic, C.; Marken, F.; Youngs, T. G. A. New bis(triazinyl) pyridines for selective extraction of americium(III). *New J. Chem.* **2006**, *30*, 1171−1183.

(36) Kolarik, Z.; Müllich, U.; Gassner, F. Selective extraction of Am(III) over Eu(III) by 2,6-ditriazolyl- and 2,6-ditriazinylpyridines 1. *Solvent Extr. Ion Exch.* **1999**, *17*, 23−32.

(37) Foreman, M. R.; Hudson, M. J.; Drew, M. G.; Hill, C.; Madic, C. Complexes formed between the quadridentate, heterocyclic molecules 6,6′-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2′-bipyridine (BTBP) and lanthanides(III): implications for the partitioning of actinides(III) and lanthanides(III). *Dalton Trans.* **2006**, *13*, 1645−1653.

(38) Geist, A.; Hill, C.; Modolo, G.; Foreman, M. R. S. J.; Weigl, M.; Gompper, K.; Hudson, M. J. 6,6′-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo(1,2,4)triazin-3-yl) (2,2′)bipyridine, an Effective Extracting Agent for the Separation of Americium(III) and Curium(III) from the Lanthanides. *Solvent Extr. Ion Exch.* **2006**, *24*, 463−483.

(39) Lavrov, H. V.; Ustynyuk, N. A.; Matveev, P. I.; Gloriozov, I. P.; Zhokhov, S. S.; Alyapyshev, M. Y.; Tkachenko, L. I.; Voronaev, I. G.; Babain, V. A.; Kalmykov, S. N.; Ustynyuk, Y. A. A novel highly

selective ligand for separation of actinides and lanthanides in the nuclear fuel cycle. Experimental verification of the theoretical prediction. *Dalton Trans.* **2017**, *46*, 10926−10934.

(40) Matveev, P. I.; Mitrofanov, A. A.; Petrov, V. G.; Zhokhov, S. S.; Smirnova, A. A.; Ustynyuk, Y. A.; Kalmykov, S. N. Testing a simple approach for theoretical evaluation of radiolysis products in extraction systems. A case of N,O-donor ligands for Am/Eu separation. *RSC Adv.* **2017**, *7*, 55441−55449.

(41) Bhattacharyya, A.; Forster, P. M.; Rego, D. B.; Czerwinski, K. R. Lanthanide Complexation of 2,6-Bis(5,6-dipyridyl-1,2,4-triazinyl)-pyridine Solvent and Lanthanide Ion Controlled Ligand Coordination Mode and Denticity. *Eur. J. Inorg. Chem.* **2016**, *6*, 921−927.

(42) Alyapyshev, M. Y.; Babain, V. A.; Antonov, N. G.; Smirnov, I. V. Extraction of americium and europium from perchloric acid solutions with N,N′-dialkyl-and N,N,N′,N′tetraalkylpyridine-2,6-dicarboxamides. *Russ. J. Appl. Chem.* **2006**, *79*, 1808−1815.

(43) Alyapyshev, M. Y.; Babain, V. A.; Tkachenko, L. I.; Paulenova, A.; Popova, A. A.; Borisova, N. E. New Diamides of 2,2′-dipyridyl-6,6′-dicarboxylic Acid for Actinide-Lanthanide Separation. *Solvent Extr. Ion Exch.* **2014**, *32*, 138−152.

(44) Zarubin, D. N.; Bushkov, N. S.; Lavrov, H. V.; Dolgushin, F. M.; Ustynyuk, N. A.; Ustynyuk, Y. A. 4,7-Di-n-butoxy-1,10-phenanthroline-2,9-dicarboxamide: a Tetradentate Ligand Featuring Excellent Solubility in Nonpolar Media. *Ineos. Open.* **2019**, *2*, 130−133.

(45) Healy, M. R.; Ivanov, A. S.; Karslyan, Y.; Bryantsev, V. S.; Moyer, B. A.; Jansone-Popova, S. Efficient Separation of Light Lanthanides(III) by Using Bis-Lactam Phenanthroline Ligands. *Chem. - Eur. J.* **2019**, *25*, 6326−6331.

(46) Borisova, N. E.; Kostin, A. A.; Reshetova, M. D.; Lyssenko, K. A.; Belova, E. V.; Myasoedov, B. F. The structurally rigid tetradentate N,N′,O,O′-ligands based on phenanthroline for binding of f-elements: The substituents vs. structures of the complexes. *Inorg. Chim. Acta* **2018**, *478*, 148−154.

(47) Ren, P.; Huang, P. W.; Yang, X. F.; Zou, Y.; Tao, W. Q.; Yang, S. L.; Liu, Y. H.; Wu, Q. Y.; Yuan, L. Y.; Chai, Z. F.; Shi, W. Q. Hydrophilic Sulfonated 2,9-Diamide-1,10-phenanthroline Endowed with a Highly Effective Ligand for Separation of Americium(III) from Europium(III): Extraction, Spectroscopy, and Density Functional Theory Calculations. *Inorg. Chem.* **2021**, *60*, 357−365.

(48) Ekberg, C.; Fermvik, A.; Retegan, T.; Skarnemark, G.; Foreman, M. R. S.; Hudson, M. J.; Englund, S.; Nilsson, M. An overview and historical look back at the solvent extraction using nitrogen donor ligands to extract and separate An(III) from Ln(III). *Radiochim. Acta* **2008**, *96*, 225−233.

(49) Kolarik, Z. Complexation and Separation of Lanthanides(III) and Actinides(III) by Heterocyclic N-Donors in Solutions. *Chem. Rev.* **2008**, *108*, 4208−4252.

(50) Hudson, M. J.; Harwood, L. M.; Laventine, D. M.; Lewis, F. W. Use of soft heterocyclic N-donor ligands to separate actinides and lanthanides. *Inorg. Chem.* **2013**, *52*, 3414−3428.

(51) Dehaudt, J.; Williams, N. J.; Shkrob, I. A.; Luo, H.; Dai, S. Selective separation of trivalent f-ions using 1,10-phenanthroline-2,9-dicarboxamide ligands in ionic liquids. *Dalton Trans.* **2016**, *45*, 11624−11627.

(52) Wu, Q. Y.; Song, Y. T.; Ji, L.; Wang, C. Z.; Chai, Z. F.; Shi, W. Q. Theoretically unraveling the separation of Am(III)/Eu(III): insights from mixed N,O-donor ligands with variations of central heterocyclic moieties. *Phys. Chem. Chem. Phys.* **2017**, *19*, 26969−26979.

(53) Gans, P.; Sabatini, A.; Vacca, A. Investigation of equilibria in solution. Determination of equilibrium constants with the HYPERQUAD suite of programs. *Talanta* **1996**, *43*, 1739−1753.

(54) Alderighi, L.; Gans, P.; Ienco, A.; Peters, D.; Sabatini, A.; Vacca, A. Hyperquad simulation and speciation (HySS): a utility program for the investigation of equilibria involving soluble and partially soluble species. *Coord. Chem. Rev.* **1999**, *184*, 311−318.

(55) Wilden, A.; Modolo, G.; Schreinemachers, C.; Sadowski, F.; Lange, S.; Sypula, M.; et al. Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of CyMe$_4$BTBP and TODGA as 1-cycle SANEX Solvent. *Solvent Extr. Ion Exch.* **2013**, *31*, 519−537.

(56) Magnusson, D.; Geist, A.; Wilden, A.; Modolo, G. Direct Selective Extraction of Actinides(III) from PUREX Raffinate Using a Mixture of CyMe$_4$-BTBP and TODGA as 1-cycle SANEX Solvent PART II: Flow-sheet Design for a Counter-Current Centrifugal Contactor Demonstration Process. *Solvent Extr. Ion Exch.* **2013**, *31*, 1−11.

(57) Xu, L.; Pu, N.; Ye, G.; Xu, C.; Chen, J.; Zhang, X.; Lei, L.; Xiao, C. Unraveling the complexation mechanism of actinide(III) and lanthanide(III) with a new tetradentate phenanthroline-derived phosphonate ligand. *Inorg. Chem. Front.* **2020**, *7*, 1726−1740.

(58) Afsar, A.; Laventine, D.; Harwood, L.; Hudson, M.; Geist. Utilizing electronic effects in the modulation of BTPhen ligands with respect to the partitioning of minor actinides from lanthanides. *Chem. Commun.* **2013**, *49*, 8534−8536.

(59) Fang, Y.; Yuan, X.; Wu, L.; Peng, Z.; Yuan, L.; et al. Ditopic CMPO-pillar[5]arenes as unique receptors for efficient separation of americium(III) and europium(III). *Chem. Commun.* **2015**, *51*, 4263−4266.

(60) Xu, L.; Zhang, A.; Lu, Y.; Yang, H.; Liu, Z. A phenanthroline-derived ligand and its complexation with Pd(II): from ligand design, synthesis and Pd(II) complexes structures to its application. *RSC Adv.* **2016**, *6*, 99859−99866.

(61) Xu, L.; Pu, N.; Sun, T.; Li, Y.; Wei, P.; Chen, J.; Xu, C. Complexation of Pu(VI) with N,N,N′,N′-tetramethyl-3-oxa-glutaramide (TMOGA) and related ligands: optical properties and coordination modes. *Dalton Trans.* **2018**, *47*, 15246−15253.

(62) Mitrofanov, A. Y.; Rousselin, Y.; Guilard, R.; Brandès, S.; Bessmertnykh-Lemeune, A. G.; Uvarova, M. A.; Nefedov, S. E. Copper(II) complexes with phosphorylated 1,10-phenanthrolines: from molecules to infinite supramolecular arrays. *New J. Chem.* **2016**, *40*, 5896−5905.

(63) Borisova, N. E.; Kharcheva, A. V.; Patsaeva, S. V.; Korotkov, L. A.; Bakaev, S.; Reshetova, M. D.; Lyssenko, K. A.; Belova, E. V.; Myasoedov, B. F. Hard-and-soft phosphinoxide receptors for f-element binding: structure and photophysical properties of europium(III) complexes. *Dalton Trans.* **2017**, *46*, 2238−2248.

(64) Premkumar, T.; Govindarajan, S.; Rath, N. P.; Manivannan, V. New nine and ten coordinated complexes of lanthanides with bidentate 2-pyrazinecarboxylate containing hydrazinium cation. *Inorg. Chim. Acta* **2009**, *362*, 2941−2946.

(65) Jansone-Popova, S.; Ivanov, A. S.; Bryantsev, V. S.; Sloop, F. V.; Custelcean, R.; Popovs, I.; Dekarske, M. M.; Moyer, B. A. Bis-lactam-1,10-phenanthroline (BLPhen), a New Type of Preorganized Mixed N,O-Donor Ligand That Separates Am(III) over Eu(III) with Exceptionally High Efficiency. *Inorg. Chem.* **2017**, *56*, 5911−5917.

(66) Lv, L.; Chen, B. H.; Liu, J.; Chen, J.; Xu, C.; Yang, Y. A structural and thermodynamic study of the complexes of U(VI) with azinecarboxylates. *Dalton Trans.* **2019**, *48*, 566−577.

(67) Dan, D.; Celis-Barros, C.; White, F. D.; Sperling, J. M.; Albrecht-Schmitt, T. E. Origin of Selectivity of a Triazinyl Ligand for Americium(III) over Neodymium(III). *Chem. - Eur. J.* **2019**, *25*, 3248−3252.