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Effect of the Introduction of Amide Oxygen into 1,10-Phenanthroline on the Extraction and Complexation of Trivalent Lanthanide in Acidic Condition

T. Kobayashi,[1,2] T. Yaita,[1,2] S. Suzuki,[1] H. Shiwaku,[1] Y. Okamoto,[1] K. Akutsu,[1,2] Y. Nakano,[2] and Y. Fujii[2]

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The extractability and complexation properties of lanthanides with *N*-alkyl-*N*-phenyl-1,10-phenanthroline-2-carboxamide were investigated. These ligands, which contain two aza-aromatic donors and an oxygen donor in a molecule, are newly developed extractants for actinides and lanthanides. *N*-Octyl-*N*-tolyl-1,10-phenanthroline-2-carboxamide exhibited high extractability of Eu^{3+} even under acidic conditions. In addition, strong complexation in acidic media was confirmed by spectroscopic titration experiments. Investigation of the complexation equilibrium revealed that the presence of an oxygen donor promotes ligand coordination with lanthanides over the competing protonation reaction in acidic solution.

Keywords actinide; extraction; lanthanide; separation

INTRODUCTION

For the advancement of the nuclear fuel cycle, one of the most important goals is the efficient disposal of high-level nuclear waste (1). In particular, the separation of trivalent actinides An^{3+} and trivalent lanthanides Ln^{3+} is considered extremely difficult due to their similar chemical properties. In recent years, soft-donor ligands have received considerable attention as possible extractants for the separation of An^{3+} from Ln^{3+} since selective extractions were observed for some aza-aromatic nitrogen ligands such as TPTZ and BTP (1–6). This selectivity is attributed to the formation of a covalent bond between the actinide, which has a slightly softer character than a lanthanide, and the soft-donor ligand (7). However, most soft donor ligands are not effective for extraction of An^{3+} and Ln^{3+} from acidic solution due to protonation of nitrogen. Accordingly, the development of an An^{3+}/Ln^{3+} separation reagent that is effective even under acidic conditions is highly desirable. On the other hand, it is well known that hard oxygen donor ligands generally show high affinities for actinides and lanthanides that are categorized as hard ions. In fact, many oxygen donor ligands show high extractabilities for both An^{3+} and Ln^{3+} even in highly concentrated acidic solution (1,8–10).

To develop nitrogen-containing ligands that can effectively extract An^{3+} and/or Ln^{3+} from even highly concentrated acidic solution, the combination of both nitrogen donors and oxygen donors has been proposed, which would allow both high extractability and high selectivity for An^{3+}. Bearing this in mind, we designed and synthesized a novel tridentate ligand, *N*-alkyl-*N*-phenyl-1,10-phenanthroline-2-carboxamide (PTA), which exhibits high extractability and selectivity for Am^{3+} over Eu^{3+} under acidic condition (11). In this study, we investigated the extraction and coordination properties of PTA for trivalent lanthanide in acidic solutions, and discuss the effects of combining both nitrogen and oxygen donors in a single ligand.

EXPERIMENTAL

Materials

The ligands investigated in this study are shown in Fig. 1. *N*-Methyl-*N*-phenyl-1,10-phenanthroline-2-carboxamide (MePhPTA) and *N*-octyl-*N*-tolyl-1,10-phenan-throline-2-carboxaide (OcTolPTA) were synthesized as described in the literature (11). ^{1}H NMR ($CDCl_3$) data of the obtained ligands are as follows: MePhPTA, δ 9.2 (br, 1H), 8.2 (br d, 1H), 8.1 (br d, 1H), 7.8 (br d, 1H), 7.7–7.5 (br m, 3H), 7.2 (br, 2H), 7.1 (br, 2H), 7.0 (br, 1H), 3.7 (s, 3H); OcTolPTA, δ 9.2 (d, 1H), 8.2 (d, 1H), 8.1 (d, 1H), 7.8 (d, 1H), 7.7–7.5 (m, 3H), 7.1 (d, 2H), 6.9 (d, 2H), 4.0 (t, 2H), 2.1 (s, 3H), 1.7 (t, 2H), 1.4–1.2 (br m, 10H), 0.9

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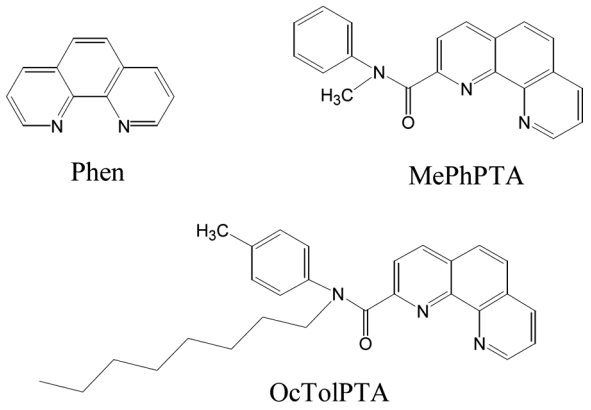

FIG. 1. Ligands investigated in this study.

(t, 3H). MePhPTA was prepared in order to investigate the chemical properties of the basic structural framework of these derivatives, and the more organo-soluble OcTolPTA was prepared for solvent extraction experiments. The other commercially available reagents used in this study were of analytical grade and used without further purification. Eu^{3+} solution for the extraction studies was prepared by diluting a standard solution of europium(III) nitrate (Wako Pure Chemical Industries, Ltd.) with nitric acid (Kanto Chemical Co., Inc.) and water; sodium hydroxide (Kanto Chemical Co., Inc.) was added to adjust the pH. Eu^{3+} solution for spectroscopic titration studies and was prepared by dissolving a weighed quantity of europium(III) chloride (Kanto Chemical Co., Inc.) in methanol and hydrochloric acid (Kanto Chemical Co., Inc.). To prepare the ligand solution, weighed quantities of MePhPTA and OcTolPTA were dissolved in methanol and chloroform, respectively.

Extraction Studies

The chloroform solution containing OcTolPTA was pre-equilibrated with an equal amount of HNO_3 solution in the absence of Eu^{3+}. An aliquot of the pre-equilibrated organic phase and an equal amount of HNO_3 solution containing 6.6×10^{-4} M Eu^{3+} were shaken for 30 min in a glass tube and then centrifuged for 10 min. This shaking time was sufficient to allow the mixture to reach equilibrium. A portion of the organic phase was transferred to another glass tube, and an equal amount of 1 M HNO_3 solution was added. The mixture was shaken for 30 min, and the Eu^{3+} in organic phase was back-extracted into the aqueous phase. The recovery of Eu^{3+} was close to 100%. The concentration of Eu^{3+} was determined by polarized Zeeman atomic absorption spectroscopy (HITACHI, Z-2300). The distribution ratio D was defined as the concentration of the Eu^{3+} in the organic phase divided by that in aqueous phase. All the extractions were performed at 298 ± 1 K.

Spectroscopic Titrations

The ligand protonation and Eu^{3+} complexation equilibria were investigated by spectroscopic titrations carried out in methanol solution. UV/vis spectra were recorded on a JASCO V-560 UV/vis spectrophotometer. The cell temperature was maintained at 298.0 ± 0.1 K by a temperature controller (JASCO ETC-505). For the measurement of ligand protonation constants, 10 μL aliquots of 2 mM HCl solution were added to 3.5 mL of solution containing 50 μM ligand using a 500 μL syringe (Hamilton, Gastight syringe 1750RN) equipped with a repeating dispenser (Hamilton PB600–1). For the measurement of the Eu^{3+} complexation constants, 10 μL aliquots of 1 mM $EuCl_3$ solution were added to 3.5 mL solution containing 50 μM ligand as described above. The absorption spectra were measured in the range from 220 to 400 nm corresponding to the absorption band of the ligand. The protonation and complexation constants were calculated by curve-fitting to the spectra, including about 40 data points for each fit, using the HYPERQUAD program (12). Wavelengths of 220–260 nm were excluded from this analysis due to strong absorption by HCl in that region. Speciation diagrams were drawn with the HySS program (13).

RESULT AND DISCUSSION

Extraction Studies

Figure 2a shows the HNO_3 concentration dependence of the D values for the extraction of Eu^{3+} from 0.01 to 5 M HNO_3 aqueous solutions by chloroform solution containing 0.5 M OcTolPTA. The distribution ratio decreases with an increase in HNO_3 concentration. This behavior is often observed for the extraction of lanthanide with a

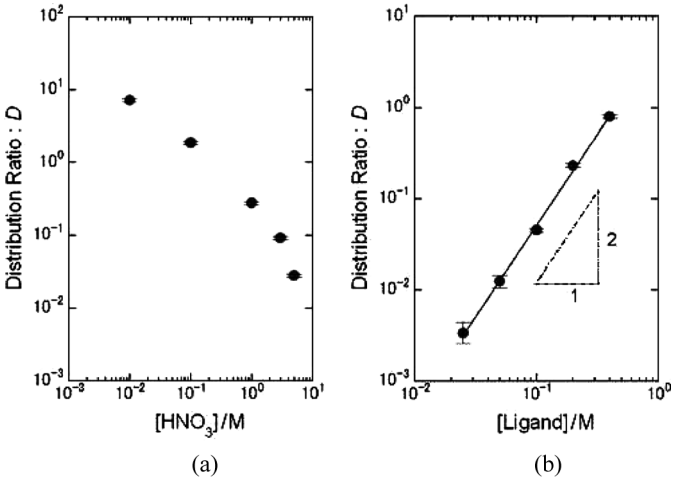

FIG. 2. (a) HNO_3 concentration dependence of distribution ratio D for Eu^{3+} extraction by 0.5 M OcTolPTA in $CHCl_3$ at 298 ± 1 K. (b) Ligand concentration dependence of distribution ratios for extraction of Eu^{3+} from 0.01 M HNO_3 by 0.02–0.4 M OcTolPTA in $CHCl_3$ at 298 ± 1 K. Curve obtained by least squares method has slope of 2.0 ($R = 0.999$).

nitrogen-donor ligand as a result of protonation of the nitrogen donor of the 1,10-phenanthroline moiety in acidic media. However, it is worth noting that most nitrogen donor ligands have rapidly decreasing extractability with lanthanides from nitric acid solutions having concentrations from 0.01 to 0.1 M, and hardly any lanthanides can be extracted from nitric acid solutions having concentrations greater than 0.1 M (3,5). In contrast, the extractability of OcTolPTA with Eu^{3+} was high even in 0.1 M HNO_3 solution. Therefore, the presence of an oxygen donor in the ligands likely promotes binding with Eu^{3+} over the competing reaction involving protonation of the ligand, resulting in high extractability even in acidic solution. A detailed discussion of the protonation and complexation behavior in acidic media is discussed later in this report.

Figure 2b shows the extractant concentration dependence of the D values for the extraction of Eu^{3+} from an aqueous 0.01 M HNO_3 solution by a chloroform solution of OcTolPTA. The distribution ratio increases with increasing extractant concentration. The following equilibrium describes the extraction of Eu^{3+} from HNO_3 solution:

$$Eu^{3+}_{aq} + nL_{org} + 3NO^{-}_{3\,aq} \rightleftharpoons EuL_n(NO_3)_{3org} \qquad (1)$$

where L denotes OcTolPTA, and the subscripts "*aq*" and "*org*" denote the "aqueous" and "organic" phases, respectively, in which the species are present. The apparent equilibrium constant is defined as:

$$K_{ex} = \frac{[EuL_n(NO_3)_3]_{org}}{[Eu^{3+}]_{aq}[L]^n_{org}[NO^-_3]^3_{aq}} \qquad (2)$$

The D is defined as follows:

$$D = \frac{[EuL_n(NO_3)_3]_{org}}{[Eu^{3+}]_{aq}} \qquad (3)$$

By introducing D into Eq. (2), the following is obtained:

$$K_{ex} = \frac{D}{[L]^n_{org}[NO^-_3]^3_{aq}} \qquad (4)$$

Taking the logarithm of both sides of equation (4), the following linear equation is obtained:

$$\log D = \log K_{ex} + n\log[L]_{org} + 3\log[NO_3]_{aq} \qquad (5)$$

The slope n obtained from curve fitting using the least squares method in Eq. (5) signifies the apparent number of extractants in the predominantly extracted species when the HNO_3 concentration is kept constant. Under these experimental conditions, the metal concentration in the organic phase is much lower than the initial ligand concentrations, and the absence of the ligand in the aqueous phase was confirmed by UV/vis spectroscopic analysis of the equilibrated aqueous phase. Thus, the ligand concentrations after equilibrium are approximately equal to the initial ligand concentrations. Accordingly, when the activity of the ligand is not considered, the slope of the curve in Fig. 2b can be regarded as the number of extractants in the predominantly extracted species. As a result, the observed slope suggests that the metal to ligand ratio in the extracted species is 1:2. A detailed discussion is included in the following section.

Spectroscopic Titrations

To discuss the competition between complexation with the metal ion and protonation of the ligand, the Eu^{3+} complexation constants with MePhPTA and the protonation constants of the ligand in methanol solution were determined by spectroscopic titration experiments. The spectral changes in the MePhPTA-H^+ and MePhPTA-Eu^{3+} systems are shown in Figs. 3a and 3b, respectively. The

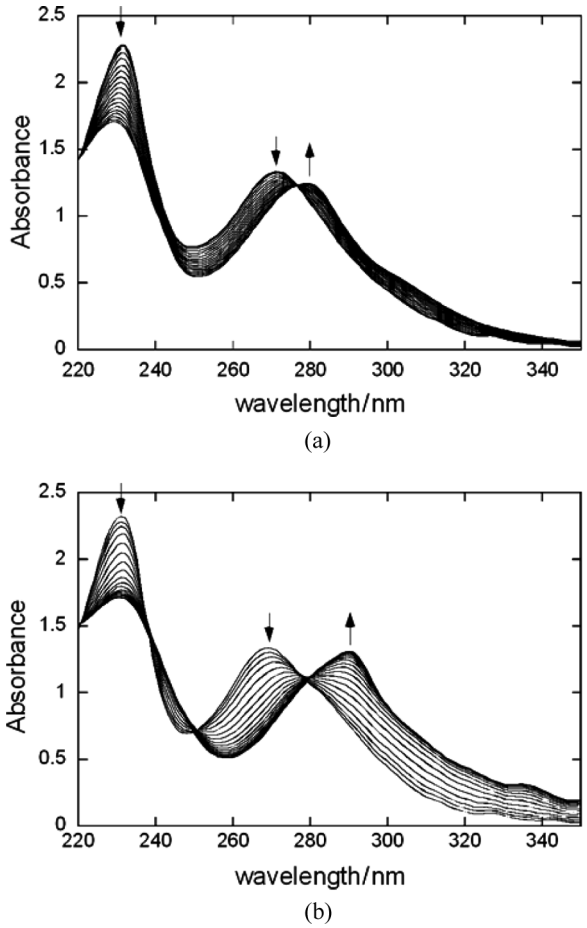

FIG. 3. Changes in absorption spectra of MePhPTA in methanol upon titration with HCl or $EuCl_3$. (a) MePhPTA-H^+ system; final spectrum corresponds to ratio of $[H^+]/[MePhPTA] = 2.0$. (b) MePhPTA-Eu^{3+} system; final spectrum correspond to ratio of $[Eu^{3+}]/[MePhPTA] = 1.0$.

TABLE 1
Logarithm of protonation and Eu^{3+} complexation constants of MePhPTA and Phen at 298 ± 0.1 K

	log K_{LH}	log β_{ML}	log β_{ML2}
MePhPTA	4.31	6.95	12.11
Phen	4.93	4.23	7.45

[a] K_{LH} values for phen were taken from Ref. (13).
*Experimental errors were less than 5% of these values.

absorption bands at 270 nm decreases with increasing H^+ and Eu^{3+} concentration, while the absorption at 280 nm for the MePhPTA-H^+ system and at 290 nm for the MePhPTA-Eu^{3+} system increases. The protonation and complexation constants were calculated by curve-fitting to plots of absorbance value at 280 nm for MePhPTA-H^+ system and at 290 nm for MePhPTA-Eu^{3+} system. The protonation constants and Eu^{3+} complexation constants with MePhPTA are defined by the following equilibrium reactions (6)–(8), as shown in Table 1.

$$K_{LH} = \frac{[(MePhPTA)H^+]}{[MePhPTA][H^+]} \quad (6)$$

$$\beta_{ML} = \frac{[Ln(MePhPTA^{3+})]}{[Ln^{3+}][MePhPTA]} \quad (7)$$

$$\beta_{ML2} = \frac{[Ln(MePhPHA)_2^{3+}]}{[Ln^{3+}][MePhPTA]^2} \quad (8)$$

The speciation model for the MePhPTA-Eu^{3+} system, which produces the best fit to the experimental data, involves two complex species with metal to ligand ratios of 1:1 and 1:2. The speciation diagrams derived from the calculated stability constants are shown in Figs. 4 and 5. Figure 4 shows the species diagram as a function of ligand/metal ratio under conditions of 6.6×10^{-4} M Eu^{3+} and pH 2.0. When the ligand to metal ratio is greater than 2, most of the Eu^{3+} forms a 1:1 or 1:2 complex. When this ratio is greater then 30, that is, when there is a large excessive of ligand relative to metal ion, most of the Eu^{3+} exists as the 1:2 metal ligand complex. This result agrees with the experimental observations regarding the extracted species, as mentioned previously. Figure 5 shows the H^+ concentration dependence of species diagram under the conditions of 6.6×10^{-4} M Eu^{3+} and 30 equiv of MePhPTA. At lower acid concentrations, the dominant species is the 1:2 complex based on the metal to ligand ratio, and this species gradually decreases with changing acid concentration from 0.01 to 10 M due to protonation of the ligand.

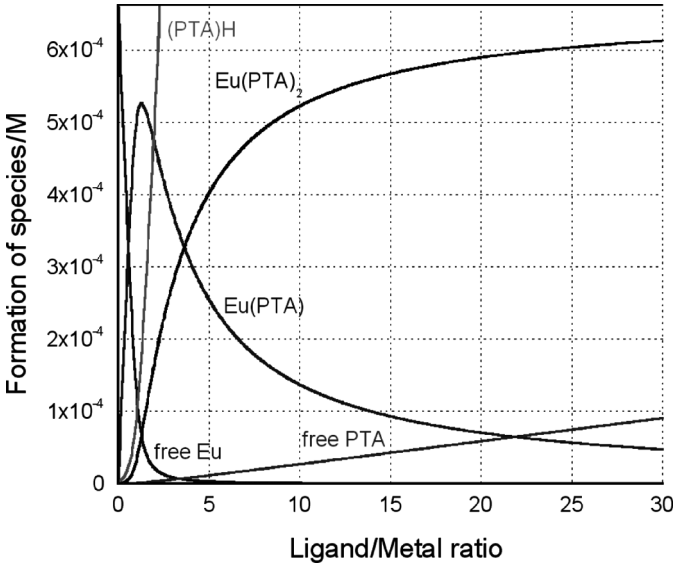

FIG. 4. Speciation diagram of Eu^{3+}-MePhPTA complex as a function of ligand/metal ratio (6.6×10^{-4} M Eu^{3+}, pH 2.0, 298 ± 0.1 K).

This behavior is similar to that of the D values in the biphasic system shown in Fig. 2a.

Effects of Oxygen Donor on Complexation in Acidic Media

To investigate the effects of the oxygen donor in PTA, the stability constants for 1,10-phenanthroline (phen), which does not include oxygen donors, were also

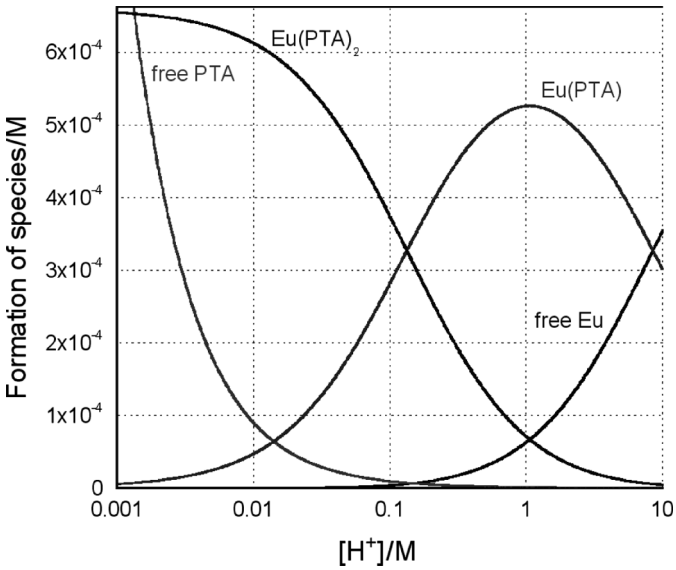

FIG. 5. Speciation diagram of Eu^{3+}-MePhPTA complex as a function of H^+ concentration (6.6×10^{-4} M Eu^{3+}, 1.98×10^{-2} M MePhPTA, 298 ± 0.1 K).

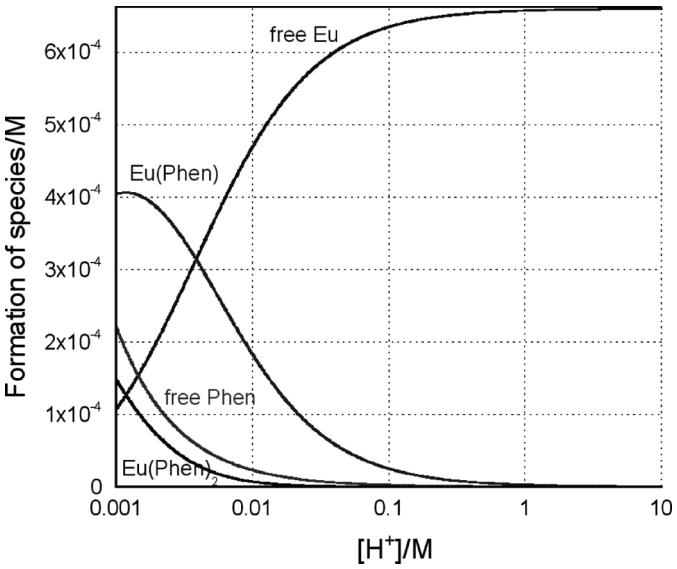

FIG. 6. Speciation diagram of Eu^{3+}-Phen complex as a function of H^+ concentration (6.6×10^{-4} M Eu^{3+}, 1.98×10^{-2} M Phen, 298 ± 0.1 K).

determined using the methods described above. The results are listed in Table 1. The log K_{LH} values of MePhPTA and Phen are very close, indicating that the introduction of the amide group does not cause any significant changes in the protonation properties of the system. In contrast, log β_{ML} and log β_{ML2} of MePhPTA are sufficiently higher than those of Phen. These results clearly indicate that the amide oxygen of the PTA acts as a coordinative donor ligand and improves coordination of the ligand to Eu^{3+} compared to Phen. The strong complexation of PTA in highly acidic conditions was confirmed from the speciation diagrams of Eu^{3+}-MePhPTA and Eu^{3+}-Phen under acidic condition, as shown in Figs. 5 and 6. In the Eu^{3+}-Phen system, the $Eu(Phen)_2$ species drastically decreases as the acid concentration changes from 0.001 to 0.01 M, and this species is not observed in acidic solution having concentrations greater than 0.1 M. In constant, the $Eu(PTA)_2$ species in the Eu^{3+}-MePhPTA system, which is the dominant extracted species in the Eu^{3+}-OcTolPTA extraction system, gradually decreases as acid concentration changes from 0.01 to 10 M, and this species is clearly observed even at an acid concentration of 1 M. These diagrams are useful for understanding the complexation behavior in the system, and also demonstrate the effect of the oxygen donor in the ligand on complexation in acidic solution. Here, the oxygen donor of PTA promotes binding with Eu^{3+} over the competing protonation reaction. Thus, the good extractability of OcTolPTA with Eu^{3+} from highly concentrated acidic solution is attributable to the effects of the oxygen donor atom.

CONCLUSIONS

The extractability and the complexation properties of Eu^{3+} with *N*-alkyl-*N*-phenyl-1,10-phenanthroline-2-carboxamide, which includes two aza-aromatic donors and an oxygen donor in a single molecule were investigated. OcTolPTA can extract Eu^{3+} well even under acidic conditions, while general aza-aromatic donor ligands are ineffective at extracting lanthanides under such conditions. The extracted species was determined to be a 1:2 metal–ligand complex based on the slope analysis of the extraction experiment. Spectroscopic titration studies also suggested that this complex is the dominant species. Furthermore, an investigation of speciation revealed that the presence of an oxygen donor in the PTA promotes binding between the ligand and Eu^{3+} over the competing reaction of ligand protonation. Therefore, this class of ligands exhibit high extractabilities for lanthanides even in highly concentrated acid solutions.

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was synthesized by oxidation of the methyl group using $KMnO_4$ in sulfuric acid solution. After the corresponding acid chloride compound was obtained by treatment of 1,10-phenanthroine-2-carboxylic acid with thionyl chloride, the reaction with secondary amine gave the target amide compounds. Distribution ratio for the extraction of Am^{3+} from 0.01 and 3 M HNO_3 aqueous solutions by 0.5 M OcTolPTA/chloroform solution are 361.4 and 1.5, respectively. The separation factor for Am^{3+} over Eu^{3+} in condition of 0.01 M HNO_3 is 51. Detailed information for ligand synthesis and actinide extraction was described in another literature under preparation.

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