Extraction and Complexation Studies of *N*-methyl-*N*-phenyl-2-(1*H*-benzimidazol-2-yl)pyridine-6-carboxamide with Trivalent Lanthanide

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The extractability and complexation properties of trivalent lanthanides with *N*-methyl-*N*-phenyl-2-(1*H*-benzimidazol-2-yl)pyridine-6-carboxamide (MePhBIZA) were investigated. The MePhBIZA, containing two aza-aromatic donors and an oxygen donor in the molecule, was designed with regard to 2-(2-pyridyl)benzimidazole (Biz) and newly synthesized as an extractant for trivalent lanthanides, Ln³⁺, and actinides, An³⁺. The MePhBIZA exhibited satisfactory extractability of Eu³⁺ even under acidic conditions. A speciation diagram, based on the formation constants determined by spectroscopic titration experiments, indicated that the MePhBIZA formed complexes with Eu³⁺ in acidic solution. These results showed that the addition of the amide group promotes ligand coordination with Eu³⁺ over the competing protonation reaction in relatively acidic solution in comparison with Biz.

1. Introduction

The next generation of the nuclear fuel cycle is aiming at efficient disposal of high-level nuclear waste (HLW) as one of the most important goals [1]. In particular, the separation of trivalent actinides (An³⁺) from trivalent lanthanides (Ln³⁺) is really important from the viewpoint of partitioning and transmutation strategy. However, this separation is considered very difficult due to the similarities in their chemical properties. In recent years, there have been several extractants based on some aza-aromatic nitrogen ligands such as TPTZ, BTP, and Biz [1-6]; consequently soft-donor ligands have received

considerable attention as possible extractants for the separation of An^{3+} from Ln^{3+} . This selectivity is attributed to the formation of weak covalent bonds between the actinides, which have a softer character than the lanthanides, and a soft-donor ligand [7]. On the other hand, most of the soft donor ligands in acidic solution considered for this process, do not often work effectively for the extraction of An^{3+} and Ln^{3+} due to protonation of the nitrogen present in aza-aromatic donors. Therefore, the development of an An^{3+} / Ln^{3+} separation reagent is highly desirable for effective extraction even under acidic conditions.

Since both the An^{3+} and Ln^{3+} are categorized as hard ions, hard oxygen donor ligands generally show high affinities for these 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]. Hence, to develop an effective extraction method of An^{3+} from Ln^{3+} , or both the An^{3+} and Ln^{3+} , by extraction with soft donor ligands from even relatively concentrated acidic solution, the combination of both nitrogen donors and oxygen donors has been proposed, which would allow high selectivity and high extractability. Accordingly, in this study, we investigated the extraction and complexation properties of a newly developed tridentate ligand, *N*-methyl-*N*-phenyl-2-(1*H*-benzimidazol-2-yl)pyridine-6-carboxamide (MePhBIZA) for Ln^{3+} , and discussed the effects of combining both nitrogen and oxygen donors in a ligand. This paper focuses on the elucidation of the improvement in extractability, not selectivity for An^{3+} , using MePhBIZA for trivalent ions, so a study on Ln^{3+} extraction only was carried out.

Figure1. Structure of Biz and MePhBIZA.

2. Experimental

2.1 Materials

All materials and chemicals were of analytical grade and used as purchased without further purification.

The synthesis of MePhBIZA is as follows. 2-(1*H*-benzimidazol-2-yl)pyridine-6-carboxylic acid (BIZCA) was synthesized and the amidation of BIZCA were performed using literature methods with minor modifications [11]. A mixture of BIZCA (5.14 g, 21.5 mmol) and thionyl chloride (28.8 g, 242.0 mmol) was refluxed for 12 h. The mixture was evaporated and the solid residue was dissolved in DMF (30 mL). *N*-Methylaniline (23.7 g, 221.5 mmol) was added to the solution and the mixture was stirred at 100 °C for 12 h. After cooling, the mixture was adjusted to a basic pH by addition of NaOH and then evaporated to dryness. The resulting residue was dissolved in ethyl acetate (40 mL). The solution was washed three times with distilled water (40 mL), and then the organic phase was evaporated. The crude residue was purified by column chromatography (silica gel, ethyl acetate) and then crystallized from a chloroform/*n*-hexane mixture to give MePhBIZA (1.56 g, 18.5 %): 1H -NMR in $CDCl_3$ (300 MHz, TMS): δ 3.52 (3H, s), 7.17-7.44 (8H, m), 7.77-7.90 (3H, m), 8.23 (1H, d, $J=7.8$), 9.19 (1H, br s). Anal. Calcd for $C_{20}H_{16}N_4O$.

0.5CHCl₃•0.25H₂O: C, 62.72; H, 4.36; N, 14.27. Found: C, 62.92; H, 4.23; N, 13.89.

The Eu³⁺ solution for the spectroscopic titration studies was prepared by dissolving europium (III) chloride (Kanto Chemical Co., Inc.) in methanol and hydrochloric acid (Kanto Chemical Co., Inc.). Regarding the extraction study, the preparation of the Eu³⁺ solution for this will be described in the extraction studies section.

To prepare the ligand solutions, MePhBIZA was dissolved in chloroform for the solvent extraction experiments. On the other hand, the ligand solutions for the titration experiments were prepared by dissolving MePhBIZA and Biz in methanol because Biz and europium (III) chloride do not dissolve in chloroform. Strictly, although there might be differences sometimes in the solvation structure of the lanthanides methanol and chloroform, these two systems could be evaluated by comparison of the coordination abilities between MePhBIZA and Biz for trivalent lanthanides, because these ligands in this study were sufficiently stronger than the solvents.

2.2 Extraction studies

In this study, determination of the distribution ratio (*D*) was determined using a radioactive tracer in order to obtain more precise *D* values. A tracer solution of ¹⁵²Eu (42 Bq/mL) was prepared by diluting with a 0.01 M HNO₃ solution. The aqueous solution was prepared by mixing a 1.0 M NH₄SCN solution and an aliquot of tracer solution. NH₄SCN was added to confirm the effect of introduction of an amide group into Biz for comparison with the extraction study with Biz alone [2]. In addition, an HNO₃ or NH₃ aqueous solution was added to adjust the pH of the aqueous solution. The organic solution was prepared by dissolving about 0.42 M MePhBIZA in chloroform. Equal volumes of the organic and aqueous solutions were mixed and shaken at 298 K for 30 min. Then, these mixtures were centrifuged for 10 min. The equilibrium pH of the aqueous phase was measured using a pH meter (HORIBA pH METER F-22). The distribution ratios were determined by γ -ray counting of ¹⁵²Eu in both phases (SEIKO EG&G MCA7600 Multi-channel Analyzer). The energy used was 121.78 keV for ¹⁵²Eu. The counting errors were almost within 1 % except for several data and the plotted points in the figures expressed most of the upper limit of each error bar.

2.3 Spectroscopic titrations

The ligand protonation and Eu³⁺ complexation equilibria were investigated by spectroscopic titrations in methanol solution. The UV/vis spectra were recorded on a JASCO V-560 UV/vis spectrophotometer. The cell temperature was maintained at 298.0 $\pm$ 0.1 K by a temperature controller (JASCO ETC-505). For the measurement of ligand protonation constants, 10 μ L aliquots of 5 mM HCl solution were added to 3.5 mL of solution containing 100 μ M ligand using a 500 μ L syringe (Hamilton, Gastight syringe 1750RN) equipped with a repeating dispenser (Hamilton PB600-1). For the measurement of the Eu³⁺ complexation constants, 10 μ L aliquots of 1 mM EuCl₃ solution were added to a 3.5 mL

solution containing 100 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]. Speciation diagrams were drawn with the HySS program [13].

3. Results and Discussion

3.1 Extraction studies

The following equilibrium describes the extraction of Eu^{3+} from aqueous solution:

where A denotes SCN or NO_3 , the subscript ' n ' denotes the average binding number of MePhBIZA with Eu^{3+} , 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:

$$K_{\text{ex}} = \frac{[\text{Eu}(\text{MePhBIZA})_n(\text{A})_{3org}]}{[\text{Eu}^{3+}]_{aq} [\text{MePhBIZA}]_{org}^n [\text{A}^{-}]_{aq}^3} \quad (2)$$

The distribution ratio of Eu^{3+} (D) is defined as follows:

$$D = \frac{[\text{Eu}(\text{MePhBIZA})_n(\text{A})_{3org}]}{[\text{Eu}^{3+}]_{aq}} \quad (3)$$

By introduction of D into equation (2), the following is obtained:

$$K_{\text{ex}} = \frac{D}{[\text{MePhBIZA}]_{org}^n [\text{A}^{-}]_{aq}^3} \quad (4)$$

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

$$\log D = \log K_{\text{ex}} + n \log [\text{MePhBIZA}]_{org} + 3 \log [\text{A}^{-}]_{aq} \quad (5)$$

Figure 2. pH dependence of the distribution ratio D for Eu^{3+} extraction by 0.42 M MePhBIZA in CHCl_3 (this work) and 0.2 M Biz in xylene : BuOH = 3:1 [6]. The aqueous solution concentration was 1.0 M NH_4SCN , and the pH values were adjusted by addition of HNO_3 .

The slope n obtained from curve fitting using the least squares method in equation (5) signifies the apparent number of extractants in the predominantly extracted species when the NH_4SCN and HNO_3 concentrations are kept constant.

Figure 2 shows the distribution ratio of Eu^{3+} as a function of the pH value at equilibrium. The distribution ratio decreased as the acidity of the aqueous solution increased. This tendency suggests that protonation gradually occurs with an increase in the acidity of the aqueous solution. Similar observations have been reported for soft donors based ligands [2]. The D values for MePhBIZA are high compared to those for Biz, even at lower pH values. These data showed that extraction abilities are improved by the introduction of the amide group, in agreement with a previous report [14]. In addition, the slope analyses were carried out using a logarithmic scale for the initial concentration of MePhBIZA, $[\text{MePhBIZA}]_{\text{init}}$, and the initial concentration of NH_4SCN , $[\text{NH}_4\text{SCN}]_{\text{init}}$. The slope of $\log D$ versus $\log[\text{MePhBIZA}]_{\text{init}}$ or $\log[\text{NH}_4\text{SCN}]_{\text{init}}$ provides the stoichiometry for MePhBIZA and NH_4SCN with respect to Eu^{3+} in the extracted species. Figures 3 (a) and (b) show the plots of $\log D$ versus $\log[\text{MePhBIZA}]_{\text{init}}$ or $\log[\text{NH}_4\text{SCN}]_{\text{init}}$. The data revealed that the D values decrease as $[\text{MePhBIZA}]_{\text{init}}$ decreases. The plot of $\log D$ versus $\log[\text{MePhBIZA}]_{\text{init}}$ gave a straight line with a slope of 3, as shown in Figure 3 (a),

Figure 3. (a) Dependency of the distribution ratio D for Eu^{3+} extraction on the MePhBIZA concentration in CHCl_3 solutions at pH 3.6. Aqueous solutions contained 1.0 M NH_4SCN . (b) Dependency of the distribution ratio D for Eu^{3+} extraction on the NH_4SCN concentration in aqueous solutions at pH 3.6. Organic solutions contained 0.42 M MePhBIZA.

whereas the slope of $\log D$ versus $\log[\text{NH}_4\text{SCN}]_{\text{init}}$ was approximately equal to 2, suggesting that three MePhBIZA and two SCN^- ions were exhibited in the extracted species. Moreover, a NO_3^- ion would be probably present in the extraction species from the viewpoint of neutralization of the complex charge. Accordingly, the extraction equilibrium can be written as follows,

3.2 Spectroscopic titrations

To discuss the competition between complexation with the metal ion and protonation of the ligand, complex formation constants for MePhBIZA and Biz with Eu^{3+} , and the protonation constants of the ligands in methanol solution were determined by spectroscopic titration experiments. The spectral changes in the ligand- H^+ and ligand- Eu^{3+} systems are shown in Figure 4(a) and 4(b), respectively. The absorptions at 230, 260, and 320 nm decrease with increasing H^+ concentration, while the absorption at 240 nm increases. The absorption at 320 nm decreases with increasing Eu^{3+} concentration, while the absorption at 360 nm increases. On the other hand, the absorptions at 230, 270, and 330 nm decrease with increasing H^+ concentration, while the absorption at 240 nm increases. The absorptions at 230 and 320 nm decrease with

increasing Eu^{3+} concentration, while the absorption at 250 nm increases. The protonation and complexation constants were calculated by curve fitting to the plots of the absorbance variation curves at 320 nm for BIZA-H^+ , at 330 nm for Biz-H^+ , at 360 nm for BIZA-Eu^{3+} , and at 230 nm for the Biz-Eu^{3+} systems, respectively.

The protonation constants and Eu^{3+} complexation constants with BIZA (or Biz) are defined by the following equation of (7)-(10), as shown in Table 1.

$$K_a = \frac{[\text{MePhBIZA}][\text{H}^+]}{[(\text{MePhBIZA})\text{H}^+]}$$
 (7)

$$\beta_{\text{ML}} = \frac{[\text{Ln}(\text{MePhBIZA})^{3+}]}{[\text{Ln}^{3+}][\text{MePhBIZA}]}$$
 (8)

$$\beta_{\text{ML}2} = \frac{[\text{Ln}(\text{MePhBIZA})_2^{3+}]}{[\text{Ln}^{3+}][\text{MePhBIZA}]^2}$$
 (9)

$$\beta_{\text{ML}3} = \frac{[\text{Ln}(\text{MePhBIZA})_3^{3+}]}{[\text{Ln}^{3+}][\text{MePhBIZA}]^3}$$
 (10)

Table 1. Logarithm of the protonation and Eu^{3+} complex formation constants of Biz and MePhBIZA in methanol. Experimental errors were less than 5 % of these values.

Ligand	pKa	$\log\beta_{\text{ML}}$	$\log\beta_{\text{ML}2}$	$\log\beta_{\text{ML}3}$
Biz	5.56	1.79	-	-
MePhBIZA	4.83	6.22	12.2	15.6

(a)

(b)

Figure 4. Changes in the absorption spectra of MePhBIZA and Biz in methanol upon titration with HCl or EuCl₃. (a) the MePhBIZA-H⁺ and Biz-H⁺ systems; the final spectrum corresponds to a [H⁺]/[Ligand] ratio of 2.0. (b) the MePhBIZA-Eu³⁺ and Biz-Eu³⁺ systems; the final spectrum corresponds to a [Eu³⁺]/[Ligand] ratio of 2.0.

The speciation models for the MePhBIZA-Eu³⁺ system produces the best fit to the experimental data, which suggested the formation of three complexes with metal to ligand ratios of 1:1, 1:2, and 1:3. The speciation models for the Biz-Eu³⁺ complex with metal to ligand ratios of 1:1 gave the best fit to the experimental data. However, Kolarik et al found that Eu³⁺ forms 1:2 or 1:3 Biz complexes [6]. It is considered that the stability constant of the 1:2 and 1:3 complexes are too low to be determined using the spectroscopic titration method in this study. The pK_a values for MePhBIZA and Biz were determined as 4.83 and 5.56, respectively. The pK_a values of pyridine and benzimidazole are respectively 5.2 and 5.4, and the evaluated pK_a value of 4.83 was slightly low. This is probably due to the addition of an electron withdrawing group (amide group) into pyridine-ring which decreased the pK_a value.

The results of the spectroscopic titrations are listed in Table 1. The pK_a values for MePhBIZA and Biz are different, indicating that the introduction of the amide group effectively causes changes in the

protonation properties of the N-donor. In contrast, the $\log\beta_{ML}$ value for MePhBIZA is sufficiently higher than that for Biz. These results clearly indicate that the amide oxygen of MePhBIZA acts as a coordinative donor ligand and improved the coordination of the ligand to Eu^{3+} compared to Biz.

3.3 Effects of the oxygen donor on complexation in acidic media

To investigate the effects of the oxygen donor in MePhBIZA, the stability constants for MePhBIZA and Biz were determined as listed in Table 1. For elucidation of the dominating species in Eu^{3+} -ligand solutions, the speciation diagrams for the Eu^{3+} -MePhBIZA and -Biz systems as a function of pH were calculated in Figure 5(a) and 5(b), respectively. These results showed that $[\text{Eu}(\text{MePhBIZA})_3]$ was still the dominating species above pH 3, and that the amount of this species steeply decreased from pH 3 to 0 in the MePhBIZA system. However, Biz showed dissociative behavior with Eu^{3+} at acidities below pH 5. These tendencies agreed well with the extraction behavior as shown in Figure 2 and the oxygen donors in MePhBIZA work effectively in acidic solution compared to the Biz extraction behavior. In addition, Eu^{3+} forms the $\text{Eu}(\text{MePhBIZA})_3(\text{SCN})_2(\text{NO}_3)$ complex as the extracted species. On the other hand, the coordination number in the first coordination sphere of Eu^{3+} in solution is generally believed to be 9 or sometimes up to 10. The estimated coordination number in this study, however, might be more than 10 if there are three MePhBIZA ligands, two SCN^- ions, and one NO_3^- ion around Eu^{3+} . Therefore, some of the ligands including anions, estimated from the stoichiometry, might not be located in the first coordination sphere. Elucidation of this discrepancy will require the other structural studies such as EXAFS and SANS, and we are planning these studies in future work.

Figure 5. (a) Speciation diagram of the Eu^{3+} -MePhBIZA complex as a function of pH (1.0×10^{-3} M Eu^{3+} , 0.1 M MePhBIZA, pH=0-6, 298 ± 0.1 K). (b) Speciation diagram of the Eu^{3+} -Biz complex as a function of pH (1.0×10^{-3} M Eu^{3+} , 0.1 M Biz, pH=0-6, 298 ± 0.1 K).

4. Conclusion

The extractability and the complexation properties of MePhBIZA with Eu^{3+} were investigated and the effects of introduction of an amide group into Biz on the extraction and coordination behavior were

discussed. The high extractability of MePhBIZA for Eu^{3+} was confirmed compared with Biz in relatively acidic solutions. The extracted species was determined as a 1:3:2:1 complex for the metal-MePhBIZA- SCN^- - NO_3^- ratios based on the slope analyses and complex formation constants. The data also revealed that the presence of an oxygen donor in MePhBIZA promoted the ligation between the MePhBIZA and Eu^{3+} over the competing protonation reaction of the ligand. Accordingly, MePhBIZA exhibits significant extractabilities for lanthanides even in acidic solutions.

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References

- 1) C. Madic, M. Lecomte, P. Baron, B. Boullis, *C. R. Physique.*, **3**, 797-811 (2002).
- 2) Z. Kolarik, *Chem. Rev.*, **108**, 4208-4252 (2008).
- 3) P. Y. Cordier, C. Hill, P. Baron, C. Madic, M. J. Hudson, J. O. Liljenzin, *J. Alloys. Compd.*, **271**, 738-741 (1998).
- 4) M. G. B. Drew, M. J. Hudson, P. B. Iveson, C. Madic, M. L. Russell, *J. Chem. Soc., Dalton Trans.*, **16**, 2711-2720 (2000).
- 5) Z. Kolarik, U. Mullich, F. Gassner, *Solvent Extr. Ion Exch.*, **17**, 1155-1170 (1999).
- 6) Z. Kolarik, U. Mullich, *Solvent Extr. Ion Exch.*, **15**, 361-379 (1997).
- 7) G. R. Choppin, *J. Alloys Compd.*, **344**, 55-59 (2002).
- 8) E. P. Horwitz, A. C. Muscatello, D. G. Kalina, L. Kaplan, *Sep. Sci. Technol.*, **16**, 417-437 (1981).
- 9) C. Musikas, H. Hubert, *Solv. Extr. Ion Exch.*, **5**, 877-893 (1987).
- 10) Y. Sasaki, Y. Sugo, S. Suzuki, S. Tachimori, *Solv. Extr. Ion Exch.*, **19**, 91-103 (2001).
- 11) C. Piguet, J. C. G. Bunzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, *J. Am. Chem. Soc.* **118**, 6681-6697 (1996).
- 12) P. Gans, A. Sabatini, A. Vacca, *Talanta*, **43**, 1739-1753 (1996).
- 13) L. Alderighi, P. Gans, A. Ienco, D. Peters, A. Sabatini, A. Vacca, *Coord. Chem. Rev.* **184**, 311-318 (1999).
- 14) T. Kobayashi, T. Yaita, S. Suzuki, H. Shiwaku, Y. Okamoto, K. Akutsu, Y. Nakano, Y. Fujii, *Sep. Sci. Tech.* **45**, 2431-2436 (2010).