

Extraction Behavior of Rare-earth Elements Using a Mono-alkylated Diglycolamic Acid Extractant

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Liquid–liquid extraction of rare-earth (RE) cations has been investigated using *N*-dodecyldiglycolamic acid (C₁₂DGAA) with a secondary amide group, and compared with that using *N,N*-dioctyldiglycolamic acid (DODGAA) with a tertiary amide group. C₁₂DGAA enables quantitative transfer of all RE cations from moderately acidic solution, while being selective toward the heavier RE cations, and performs better than typical carboxylic-acid-type extractants. However, C₁₂DGAA provides low extraction performance and separation ability for RE cations compared with DODGAA because of the weaker basicity of the amide oxygen. Slope analysis demonstrated that RE³⁺ transfer with C₁₂DGAA proceeded through a proton-exchange reaction, forming a 1:3 complex, RE(C₁₂DGAA)₃. Structural characterization by X-ray diffraction revealed that three *N*-butyldiglycolamic acid (C₄DGAA) molecules coordinated to the La³⁺ central ion in a tridentate fashion and the La³⁺ primary coordination sphere consisted of three oxygen atoms from the amide group, three oxygen atoms from the ether group, and three oxygen atoms from the carboxy group.

1. Introduction

Rare-earth (RE) elements are critical components of advanced materials with diverse applications. Although much effort has been devoted to the development of alternative materials to replace RE elements in recent years, they are irreplaceable in many cases because of their remarkable optical, electronic, and magnetic properties [1,2]. Industrial wastes (so-called urban mines) are promising new resources of RE elements and recycling of RE elements is of importance from an economic, industrial and environmental point of view [3-5]. However, the mutual separation of individual RE cations (RE³⁺) from each other is difficult because of their chemical similarity, *e.g.*, ionic diameter, electric charge and hardness as a Lewis acid.

Solvent extraction has been widely used as a feasible process for the separation and purification of metal ions. To date, numerous potentially attractive extractants have been developed for efficient extraction and separation of RE cations [6-9]. However, rather laborious and elaborate synthetic processes are required to obtain extractants with high extraction performance and separation ability for target RE cations,

which gives rise to a high production cost. To this day, commercial organophosphorus compounds such as di(2-ethylhexyl)phosphoric acid (D2EHPA) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A) are still generally employed in practical extraction processes as RE extractants.

Recently, we developed novel acidic tridentate chelate reagents with a diglycolamic acid (DGAA) framework, which is composed of an amide group and a carboxy group connected by an ether chain [10-16]. For example, *N,N*-dioctyldiglycolamic acid (DODGAA, Fig. 1) is somewhat analogous to *N,N,N',N'*-tetra(*n*-octyl)diglycolamide (TODGA) [17-19], but it is an ionizable Brønsted-acid-type extractant unlike the neutral Lewis-base-type TODGA. Although DODGAA can be synthesized readily in a single step and is a carboxylic-acid-type extractant consisting only of C, H, O, and N atoms, this ligand is able to provide a remarkably high extraction performance for RE³⁺ compared with typical carboxylic-acid-type extractants (*e.g.*, Versatic 10). Furthermore, the extraction performance of DODGAA is comparable to that of organophosphorus extractants (*e.g.*, D2EHPA and PC-88A) [13].

In this study, we synthesized *N*-dodecyldiglycolamic acid (C₁₂DGAA, Fig. 1) with a secondary amide group (R–NH–C=O) as an analogous extractant to DODGAA with a tertiary amide group (R–NR–C=O). The extraction behavior of all RE cations, except Pm(III), using C₁₂DGAA was compared with the extraction behavior using DODGAA to investigate the influence of the amide group on the extraction performance and coordination ability of DGAA ligands for RE cations. In addition, the structure of the La³⁺ complex formed from *N*-butyldiglycolamic acid (C₄DGAA, Fig. 1) was characterized by X-ray diffraction (XRD) to clarify the relationships between the extraction performance of DGAA ligands for RE cations and the coordination arrangement of the RE³⁺ complex.

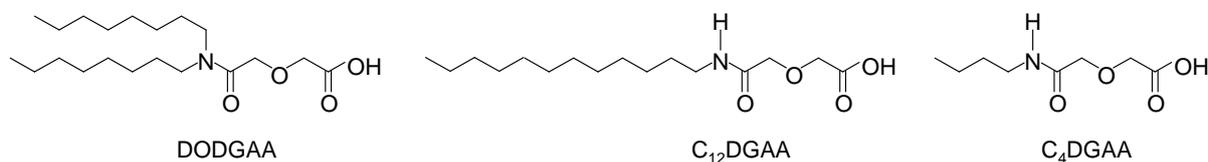


Figure 1. Molecular structures and abbreviations of extractants.

2. Experimental

2.1 Reagents

Diglycolic anhydride (Tokyo Chemical Industry Co., Ltd.), dioctylamine (Sigma-Aldrich Co.) dodecylamine (Tokyo Chemical Industry Co., Ltd.), and butylamine (Wako Pure Chemical Industries, Ltd.) were used for the synthesis of DODGAA, C₁₂DGAA, and C₄DGAA. DODGAA was synthesized according to the publish procedure [10,11,13]. RE(III) nitrates (all lanthanides except Pm(III), which is a radioactive element) were purchased from Kishida Chemical Co., Ltd. (Osaka, Japan). All other reagents were commercially available, of analytical grade, and used as received. Ultrapure water (18.2 MΩ·cm), produced using a Direct-Q system (Millipore), was used throughout this study.

2.2 Synthesis of C₁₂DGAA

Diglycolic anhydride (5.9 g, 48.3 mmol) was dispersed in dry CH₂Cl₂ (40 mL). Dodecylamine (7.7 g, 40.3 mmol) dissolved in dry CH₂Cl₂ (10 mL) was slowly added dropwise to the solution in an ice-bath. The

mixture was stirred at room temperature for more than 24 h. The resulting clear solution was washed three times with 0.1 mol/L HCl (3 × 100 mL) and water (3 × 100 mL). The organic layer was dried with anhydrous Na₂SO₄. After filtration, the solvent was removed *in vacuo* to give the crude product, which was recrystallized from *n*-hexane to obtain C₁₂DGAA as a white powder (12 g, 99% yield). ¹H NMR (400 MHz, CDCl₃, TMS, 25°C): δ 0.88 (t, 3H, N-(CH₂)₁₁-CH₃), 1.26 (s, 18H, N-CH₂-CH₂-(CH₂)₉-CH₃), 1.54 (quintet, 2H, N-CH₂-CH₂-C₁₀H₂₁), 3.29 (quartet, 2H, N-CH₂-C₁₁H₂₃), 4.14 (s, 2H, N-CO-CH₂-O), 4.20 (s, 2H, CH₂-COOH), 6.95 (t, 1H, NH), 9.59 (s, 1H, COOH). MS (MALDI-TOF) *m/z*: 302.2 [M + H]⁺. Anal. Calcd for C₁₆H₃₁O₄N₁: C, 63.75; H, 10.37; N, 4.65. Found: C, 63.51; H, 10.51; N, 4.63.

2.3 Synthesis of C₄DGAA

Diglycolic anhydride (5.0 g, 41 mmol) was dissolved in dry THF (50 mL). Butylamine (3.05 g, 41 mmol) dissolved in dry THF (10 mL) was slowly added dropwise to the solution in an ice-bath. The mixture was stirred at room temperature for 36 h. After the solvent was removed *in vacuo*, the resulting crude product was washed three times with hexane (3 × 12 mL) and was recrystallized from water to obtain C₄DGAA as a white powder (5.08 g, 65.5% yield). ¹H NMR (400 MHz, CDCl₃, TMS, 25°C): δ 0.93 (t, 3H, N-(CH₂)₃-CH₃), 1.38 (m, 2H, N-CH₂-CH₂-CH₂-CH₃), 1.53 (quintet, 2H, N-CH₂-CH₂-C₂H₅), 3.31 (quartet, 2H, N-CH₂-C₃H₇), 4.13 (s, 2H, N-CO-CH₂-O), 4.22 (s, 2H, CH₂-COOH), 6.83 (t, 1H, NH). MS (MALDI-TOF) *m/z*: 190.1 [M + H]⁺. Anal. Calcd for C₈H₁₅NO₄: C, 50.78; H, 7.99; N, 7.40. Found: C, 50.21; H, 7.90; N, 7.38.

2.4 Extraction procedure

Organic phases were prepared by dissolving C₁₂DGAA (10 mM) in isooctane containing 5 vol% 1-octanol as a solubilizer. Aqueous phases containing multiple RE cations were prepared having different pH values. To prepare each aqueous phase, stock solutions containing each RE(III) nitrate were added to a 2-morpholinoethanesulfonic acid (MES) buffer to give metal ion concentrations of 0.01 mM, and the pH was adjusted by addition of either HNO₃ or NaOH. Equal volumes of the organic and aqueous solutions were mixed and shaken mechanically at 25 °C for 30 min to attain equilibrium. After separation of the two phases by centrifugation, the metal ions in the organic phase were back-extracted into 1 M HNO₃. The concentrations of RE³⁺ in the aqueous phase and the receiving phase were determined using an inductively coupled plasma mass spectrometer (PerkinElmer NexION 300) to obtain the extractability (= [RE³⁺]_{org}/[RE³⁺]_{ini} × 100) and the distribution ratio ($D = [RE^{3+}]_{org}/[RE^{3+}]_{aq}$). The subscripts org, aq and ini denote the organic phase, the aqueous phase and the initial condition, respectively. The equilibrium pH values of the aqueous phases were also measured. For comparison, extraction tests with DODGAA were also conducted, following the same procedure, with HNO₃ solutions being used as aqueous phases.

2.5 Single-crystal X-ray structure determination

Single crystals of the La-C₄DGAA complex were prepared according to the following procedure. La(CH₃COO)₃ was dissolved in a small amount of water by heating. C₄DGAA (3 eq.), dissolved in ethanol, was added to the solution. After the solvent and generated acetic acid were removed *in vacuo*, the resulting complex was re-dissolved in ethanol. This evaporation and re-dissolution procedure was repeated until no acetic acid was produced. The resulting complex was dissolved in a mixture of ethanol and *n*-hexane by heating. Colorless crystals of the La-C₄DGAA complex were obtained by leaving the solution at room temperature over a period of several days. These crystals which were suitable for X-ray analysis were

selected and mounted on a glass fiber using highly viscous oil. Diffraction data were measured on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo-K α ($\lambda = 0.71075 \text{ \AA}$) radiation at $-94 \text{ }^\circ\text{C}$. The unit cell parameters were determined using CrystalClear from 18 images. The crystals to detector distance was ca. 45.2 mm. Data were collected using 0.5° intervals in ω to a maximum 2θ value of 55.0° . The highly redundant data sets were reduced using CrystalClear and corrected for Lorentz and polarization effects. An empirical absorption correction was applied for each complex. Structures were solved by direct methods (SHELXS2013). The position of the La(III) ions and their first coordination sphere were located from a direct method E -map; other non-hydrogen atoms were found in alternating difference Fourier syntheses, and least-squares refinement cycles and during the final cycles were refined anisotropically (CrystalStructure). Refinement was carried out by a full matrix least-squares method on F^2 . All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL97. The obtained crystallographic data are as follows: $[La(C_4DGAA)_3](H_2O)_3$ ($C_{24}H_{51}LaN_3O_{15}$), $M.W. = 760.58$, *monoclinic*, $C2/c$, $a = 25.7486(10) \text{ \AA}$, $b = 27.2080(9) \text{ \AA}$, $c = 10.153(3) \text{ \AA}$, $\beta = 95.881(9)^\circ$, $V = 7075(2) \text{ \AA}^3$, $Z = 8$. The data refinement was converged at $R_1 = 0.1136$ ($I > 2.00 \sigma(I)$), $wR_2 = 0.3549$. The goodness of fit (GOF) was 0.931. The butyl group connected to the amide nitrogen was highly disordered. We could not find any electron density around C21 after a full matrix least-squares; therefore only one carbon of the butyl group (C21) was included in the final calculations. This refinement is the best after some data collections. Moreover, hydrogen atoms of the lattice waters and one carbon (C16) were not included in the final calculations.

3. Results and Discussion

3.1 Extraction behavior of RE(III) cations with DGAA extractants

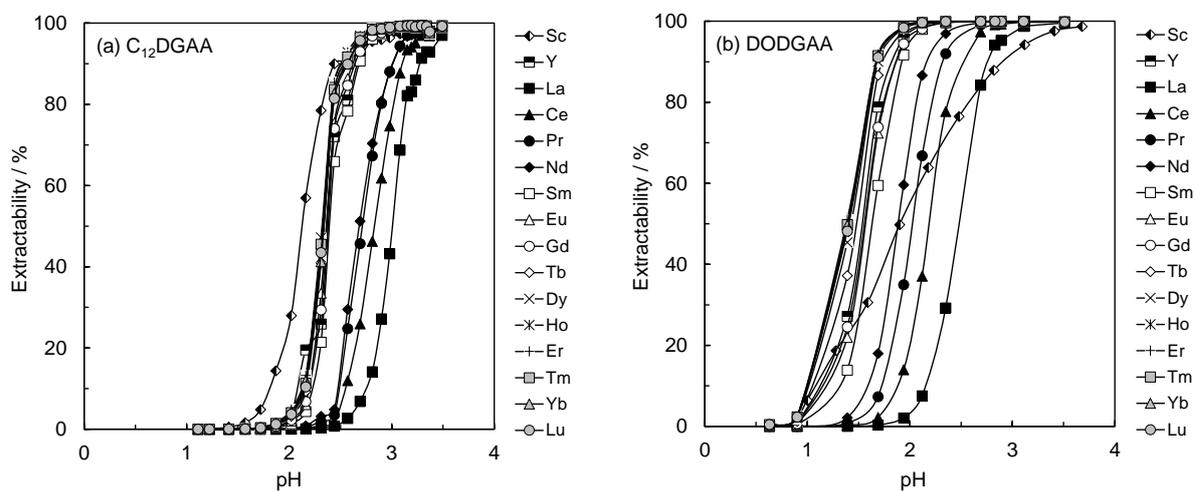


Figure 2. Extraction behavior of RE(III) cations with (a) $C_{12}DGAA$ and (b) $DODGAA$ as a function of pH in the aqueous phase. $[RE^{3+}] = 0.01 \text{ mM}$, $[\text{extractant}] = 10 \text{ mM}$. Each aqueous phase contained 16 RE(III) cations.

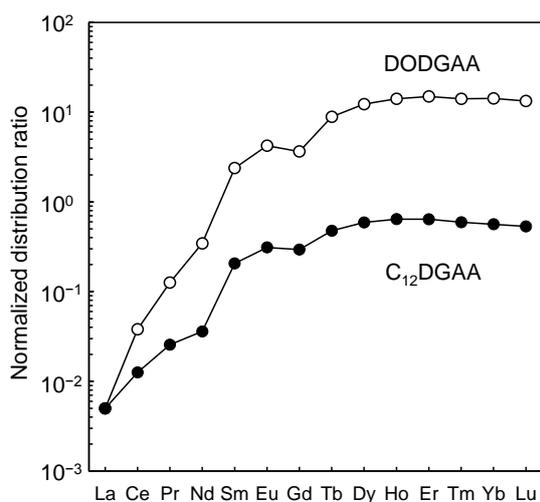
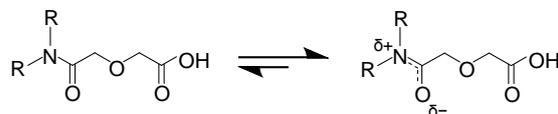


Figure 3. Selectivity of C₁₂DGAA and DODGAA for RE(III) cations. [RE³⁺] = 0.01 mM, [extractant] = 10 mM. pH 2.6 when using C₁₂DGAA, pH 1.9 when using DODGAA. The distribution ratio of RE³⁺ with C₁₂DGAA and DODGAA was normalized using the distribution ratio of La³⁺.

The extraction behavior of 16 RE(III) cations with C₁₂DGAA as a function of the aqueous-phase equilibrium pH is shown in Figure 2. The extraction performance of C₁₂DGAA was compared with that of DODGAA. The partitioning of all RE³⁺ with C₁₂DGAA into the organic phase increased with an increase in the pH. Quantitative transfer was achieved at pH ≥ 3.5 for light RE³⁺ and at pH ≥ 2.8 for middle and heavy RE³⁺. C₁₂DGAA performed better than typical carboxylic-acid-type extractants such as Versatic 10, which generally transfers RE³⁺ under neutral aqueous conditions (6 ≤ pH ≤ 7) [16,20]. This is likely attributable to the chelate effect created by the tridentate diglycolamic acid framework. In contrast, RE³⁺ transfer with C₁₂DGAA occurred in higher pH ranges than that with DODGAA, which indicates that C₁₂DGAA has a lower extraction performance for RE³⁺ than DODGAA. Although C₁₂DGAA showed the highest selectivity for Sc(III) cations among 16 RE(III) cations, DODGAA extracted Sc(III) cations across the whole range of extraction of the other RE(III) cations. Why this different extraction behavior for Sc(III) cations was observed is unclear at present, but likely involves the hydrolysis of Sc(III) cations.

The competitive extraction of RE³⁺ using C₁₂DGAA was compared with that using DODGAA to assess the selectivity (Figure 3). Aqueous phases containing 14 RE(III) cations except Sc(III) and Y(III) were employed, and the distribution ratio of RE³⁺ with C₁₂DGAA and DODGAA was normalized using the distribution ratio of La³⁺ to clarify the difference in selectivity between C₁₂DGAA and DODGAA. Both DGAA extractants exhibited selectivity for the heavier RE³⁺, probably because of the higher charge densities of the heavier RE³⁺ which facilitated electrostatic interactions with anionic C₁₂DGAA and DODGAA. Furthermore, it was found that C₁₂DGAA had much lower separation ability for RE³⁺ than DODGAA, in addition to lower extraction performance as shown in Figure 2. We suggest that the

DGAA with a tertiary amide group



DGAA with a secondary amide group

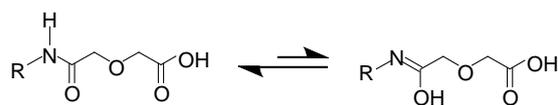


Figure 4. Tautomerism of the DGAA framework with a tertiary amide group or a secondary amide group.

difference in the extraction and separation performances between C₁₂DGAA and DODGAA is likely attributable to the difference in the basicity of the amide oxygen atom. As shown in Figure 4, the DGAA framework with a tertiary amide group (DODGAA) has a relatively rigid molecular geometry because of the partial double-bond character of the C–N bond of the amide group, which leads to a stronger basicity of the amide oxygen atom [21]. This enhanced basicity is advantageous for coordinative and electrostatic interactions with metal ions. The occurrence of the amide tautomer is confirmed by ¹H NMR measurements. In fact, the ¹H NMR signals of the N(CH₂)₂–C=O group of DODGAA are observed as two distinguishable peaks at $\delta = 3.10$ and 3.35 ppm [10,11,13]. In the case of the DGAA framework with a secondary amide group (C₁₂DGAA), it is obvious that the basicity of the amide oxygen atom is weaker than that of a tertiary amide oxygen atom. In addition, it is likely that a secondary amide group would form an intramolecular hydrogen bond with carbonyl oxygen or ether oxygen [21].

3.2 Slope analysis and structure of La–DGAA complex

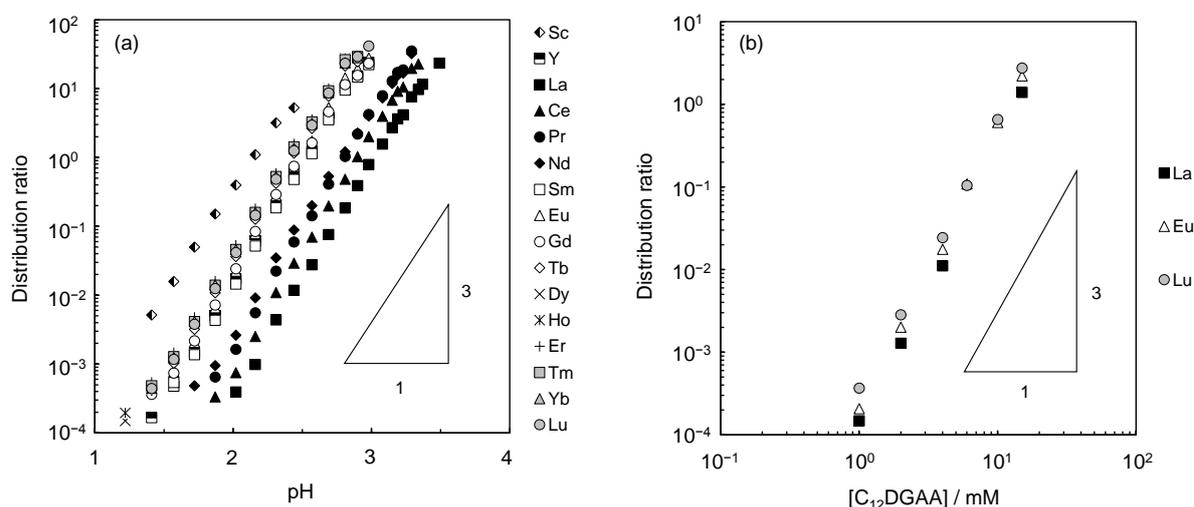


Figure 5. Slope analysis of RE(III) extraction using C₁₂DGAA. (a) Dependency on the pH of the aqueous phase: [RE³⁺] = 0.01 mM, [C₁₂DGAA] = 10 mM. Each aqueous phase contained 16 RE(III) cations. (b) Dependency on the C₁₂DGAA concentration: [La³⁺] = [Eu³⁺] = [Lu³⁺] = 0.01 mM, pH 3.0 for La³⁺, pH 2.4 for Eu³⁺, pH 2.35 for Lu³⁺.

The mechanism of RE³⁺ extraction with C₁₂DGAA was investigated by slope analysis. Figure 5(a) shows the logarithmic plots of the distribution ratios of 16 RE(III) cations with C₁₂DGAA as a function of equilibrium pH in the aqueous phase. The slopes of the logarithmic distribution ratio *versus* pH were approximately 3 for all 16 RE(III) cations, suggesting that three protons from the C₁₂DGAA molecules are released into the aqueous phase to form neutral complexes with trivalent RE(III) cations through a proton-exchange reaction. It was confirmed that the equilibrium pH values in the aqueous phases after extraction were lower than the initial pH values before extraction.

In addition, the extraction of RE(III) cations was investigated as a function of the C₁₂DGAA

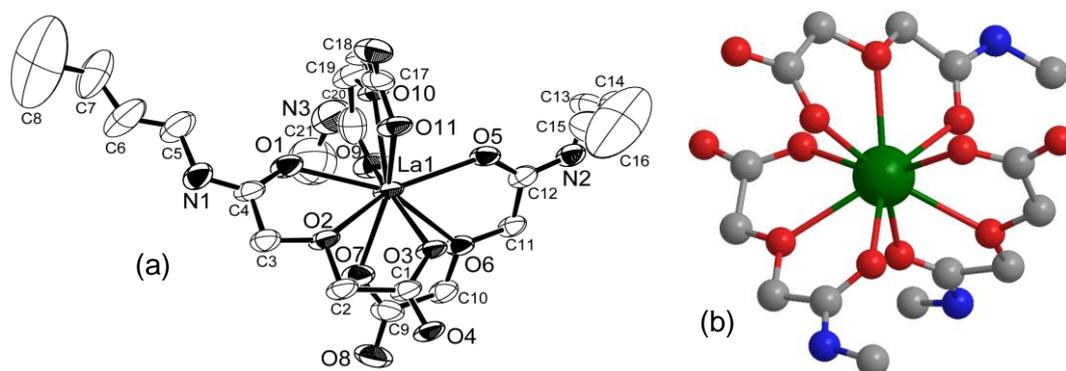


Figure 6. (a) Preliminary crystal structure of $[\text{La}(\text{C}_4\text{DGAA})_3]$ with 20% probability ellipsoids; (b) illustration of La^{3+} primary coordination sphere. La^{3+} = green; oxygen = red; nitrogen = blue; carbon = gray. Hydrogen atoms, butyl group, and H_2O molecules have been omitted for clarity.

concentration to determine the stoichiometry of the $\text{RE}-\text{C}_{12}\text{DGAA}$ complexes in the organic phases. La^{3+} , Eu^{3+} , and Lu^{3+} were used as representative light, middle, and heavy RE cations, respectively. As shown in Figure 5(b), the logarithmic plots of the distribution ratio versus the C_{12}DGAA concentration was linear with a slope of 3 for La^{3+} , Eu^{3+} , and Lu^{3+} extractions. These results indicate that three C_{12}DGAA molecules were required to extract one RE^{3+} , and a 1:3 complex, $\text{RE}(\text{C}_{12}\text{DGAA})_3$, was formed.

Typical carboxylic-acid-type and organophosphorus extractants are known to exist as dimers in non-polar organic solvents [22-25]. When the dimers are involved in RE^{3+} transfer, 1:6 discrete complexes are formed. To confirm the credibility for the formation of a 1:3 complex, i.e. $\text{RE}(\text{C}_{12}\text{DGAA})_3$, the structure of the $\text{La}-\text{DGAA}$ complex was characterized by X-ray diffraction. Unfortunately, preparation of single crystals of the La complex with C_{12}DGAA proved difficult because of the flexibility of the dodecyl chain. Thus, single crystals of the $\text{La}-\text{DGAA}$ complex were prepared using analogous C_4DGAA with a shorter alkyl chain. The crystal structure obtained is illustrated in Figure 6. The molecular formula of the crystallized complex was determined to be $[\text{La}(\text{C}_4\text{DGAA})_3](\text{H}_2\text{O})_3$. Three C_4DGAA molecules coordinated to the La^{3+} central ion in a tridentate fashion but the direct coordination of water molecules to the La^{3+} center was not observed. It is worthy of note that the dimerization of C_4DGAA and the intramolecular hydrogen bonding of the secondary amide group within the $\text{La}-\text{DGAA}$ complex were not observed. The formation of a 1:3 complex and dehydration are in good agreement with the stoichiometry determined by slope analysis and our previous results on lanthanide transfer using DODGAA [13]. The total coordination number in the La^{3+} primary coordination sphere was 9, consisting of three oxygen atoms from the amide group, three oxygen atoms from the ether group, and three oxygen atoms from the carboxy group with average coordination distances of 2.502 Å, 2.649 Å, and 2.481 Å, respectively. These results suggest that the oxygens from the amide group and the carboxy group can strongly coordinate to the La^{3+} central ion relative to the oxygens from the ether group. The $\text{La}-\text{DGAA}$ complex has a distorted tricapped trigonal prism geometry with three ether oxygen atoms capped on the three faces of the prism, and three

oxygen atoms from the amide group and three oxygen atoms from the carboxy group at the corners. Recently, a similar geometry of the RE–DGAA complex was reported by Tian *et al.* in their studies on the Nd–DGAA complex prepared by *N,N*-dimethyldiglycolamic acid with a tertiary amide group [26]. Furthermore, it is obvious that the amide nitrogen is not involved in the complex formation with La³⁺, as expected from the lower basicity of the amide nitrogen (Figure 4).

On the basis of the results obtained above, the extraction equilibrium equation for RE³⁺ transfer using C₁₂DGAA (HL) is represented as follows:



4. Conclusion

In the present study, the extraction behavior of 16 RE cations using C₁₂DGAA with a secondary amide group was investigated, and the results were compared with that obtained using DODGAA with a tertiary amide group. C₁₂DGAA is capable of quantitative partitioning of all RE cations, showing selectivity for heavier RE cations. However, the extraction performance and separation ability of C₁₂DGAA for RE cations are lower than those of DODGAA, indicating that the basicity of the amide oxygen has a great influence on the performance of the DGAA framework as a metal ligand. The structural characterization of the La–DGAA complex demonstrated that three DGAA molecules coordinated to the La³⁺ central ion in a tridentate fashion through three oxygen atoms from the amide group, three oxygen atoms from the ether group, and three oxygen atoms from the carboxy group. The present findings suggest the molecule incorporating a DGAA framework is a promising tridentate chelate ligand for RE cations. In the future, it is envisaged that modification of the DGAA framework with appropriate functional groups will lead to the development of novel extractants, and contribute to the recycling of valuable metal ions.

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