



ADSORPTION OF RARE EARTH METAL IONS ON NOVEL TRIPODAL BROOM METHYLCARBAMOYLMETHOXY- ACETIC ACID IMPREGNATED RESIN

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ABSTRACT

The novel broom methylcarbamoylemethoxy-acetic acid impregnated resin has been prepared to investigate the adsorption behavior of nine rare earth metals. The present resin demonstrates adsorption ability for rare earth metal ions. The selectivity order for rare earth series is as follows: Ho>Er>Gd>Y>Eu>Sm>>Nd>Pr>>La. This order is different from those of general carboxylic acid extractants. Maximum adsorption capacity of holmium is found to be 0.21 mol kg⁻¹. From the comparison of the reagent amount impregnated in the resin and the maximum adsorption capacity, the adsorption stoichiometry is found to be 1:2 (Ho : reagent).

Keywords: Tripodal broom compound, Impregnated resin, Adsorption, Rare earth metals, Methylcarbamoylemethoxy-acetic acid

INTRODUCTION

Various impregnated resins containing macrocyclic compounds such as crown ethers [1], cryptands [2] and calixarene [3] have been prepared. Recently, an impregnated resin containing organophosphorus extractant, PC-88A (2-ethylhexyl hydrogen 2-ethylhexylphosphonate), which

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demonstrates high adsorption and separation ability for rare earth metals has been prepared [4, 5].

The tripodal broom compound shown in Fig.1 is a very attractive and interesting host compound. It consists of alkyltrimethylol and is named as a “broom molecule” derived from the functional site at the edge of a long alkyl chain. Alkyl moiety as a “broom stick” is easily substituted by using the corresponding aldehyde as the reactant. Since high solubility into organic solvents is required for impregnation, aldehyde with longer alkyl moiety has been selected. On the other hand, a coordination site such as a “broom head” consists of three alcoholic groups simultaneously substituted with groups suitable for metal recognition. The modified tripodal broom compounds demonstrate the following characteristics: 1) C_3 symmetry based on sp^3 carbon, 2) high coordination ability due to the plural functional groups for chelate effect and preorganization, 3) efficient separation to rare earths, especially to smaller heavy earth metals due to a small rigid structure.

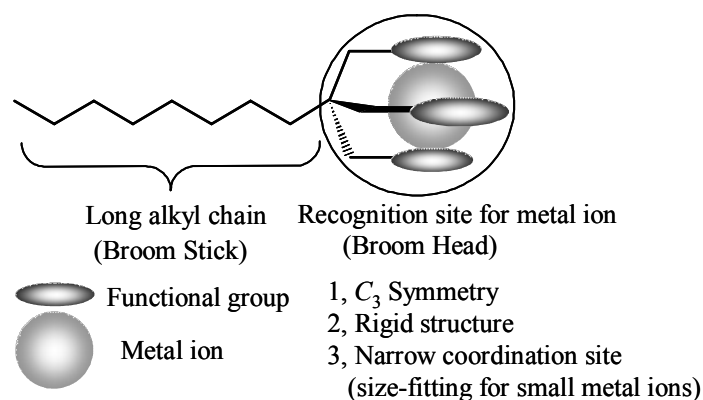


Fig. 1. Broom molecule for metal uptake.

Several tripodal compounds with a short “broom stick”, such as triamine, triether-amide, triether-ester, triether-carboxylic acid and so on, have been reported in the field of coordination and analytical chemistry [6-14]. However, no paper reports on ion-exchange resins containing the tripodal compounds. In our previous work, the introduction of three functional groups to trimethylolnonane was not successful because tri-substitution was not completed [15].

In the present work, we report on the preparation of a novel ion-exchange resin impregnating the tripodal broom compound with methylcarbamoylmethoxy-acetic acids and the investigation of adsorption behavior of rare earth metal ions.

MATERIALS / METHODS / PROCEDURES

Reagents

Chemical structures of the presented reagent and Amberlite XAD-7 are shown in Fig.2. The route of synthesis is shown in Fig.3.

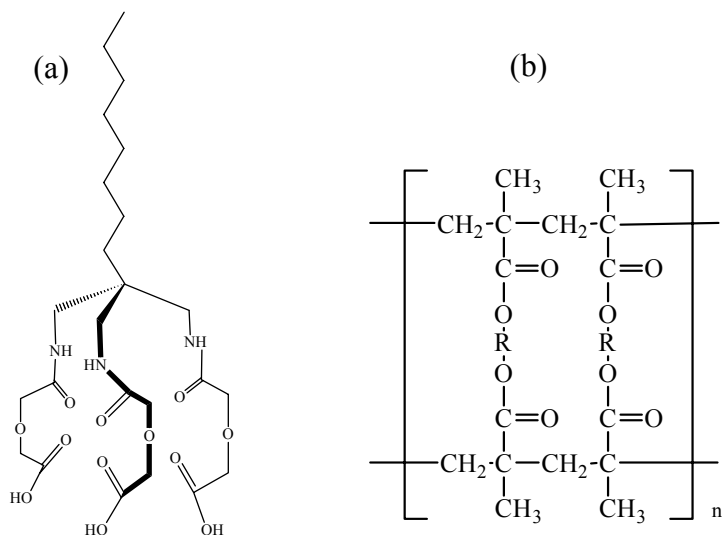


Fig. 2. Chemical structures of the presented reagent (a) and Amberlite XAD-7 (b).

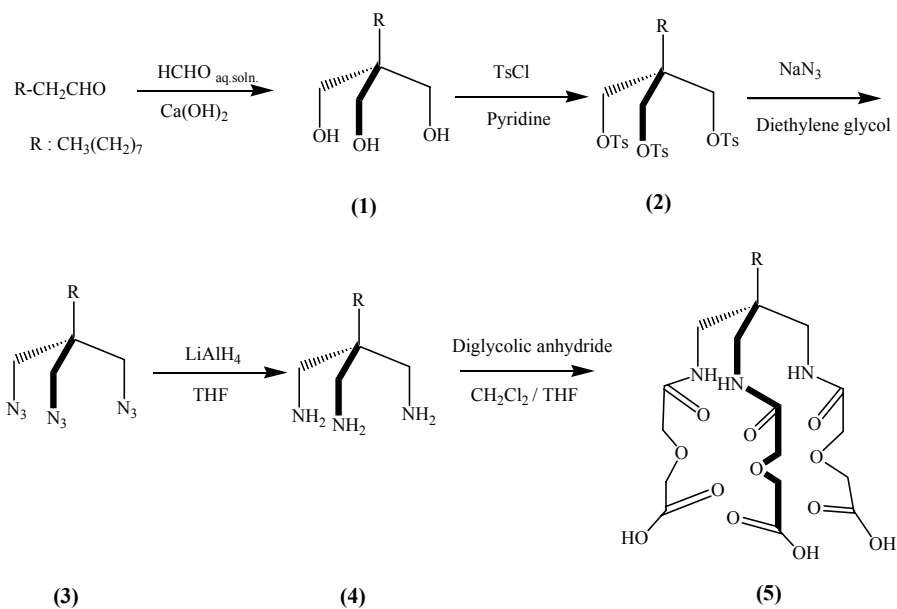


Fig. 3. Synthetic route of the presented reagent.

Synthesis of 1,1,1-tris (hydroxymethyl) nonane (1) [16]

The aqueous solution of formaldehyde (111 g, 35 wt%, 1.28 mol, 6.7 eq.) and calcium hydroxide (13.0 g, 176 mmol, 0.9 eq.) was added to the solution of *n*-decyl aldehyde (30.1 g, 193 mmol) in ethanol (25 cm³). The reaction mixture was stirred for 5 h at 328 K. After cooling to room temperature, diethyl ether was added to extract the product upon stirring, and 1 M (M = mol dm⁻³) hydrochloric acid solution was also added to neutralize the mixture. The organic and aqueous layers were collected separately, and a small portion of diethyl ether was added to the aqueous solution to extract the product. The operation was carried out more than four times. The organic solution extracted from the product was washed with saturated sodium chloride solution three times, and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated, and then *n*-heptane was added to the residue to reprecipitate the crude product. The product was recrystallized from chloroform to give white needles; yield 39.9%, FT-IR (KBr) $\nu_{\text{O-H}}$ 3370 cm⁻¹, $\nu_{\text{C-H}}$ 2955, 2926 and 2849 cm⁻¹, $\gamma_{\text{C-O}}$ 1008 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃, TMS, 303 K) δ 0.88 (3H, t, CH₃), 1.26 (14H, s, (CH₂)₇), 2.52 (3H, s, OH), 3.75 (6H, s, CH₂OH).

Synthesis of 1,1,1-tris (*p*-toluenesulfonyloxymethyl) nonane (2) [17]

p-toluenesulfonyl chloride (90.9 g, 477 mmol, 6.9 eq.) was added to the solution of **1** (15.0 g, 68.8 mmol) in pyridine (100 cm³) and stirred for 2 h in an ice bath under N₂ flow. The mixture solution was stirred for 9 days at room temperature. In order to remove pyridine as a hydrochloride salt, 6 M hydrochloric acid (100 cm³) solution was added to the mixture and stirred for 1 h in an ice bath. After stirring, chloroform was added to the mixture solution to extract the product. The organic solution was washed three times with 1 M hydrochloric acid solution, and saturated sodium chloride solution, and thereafter dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated, and then white crude product was dried *in vacuo*. The product was recrystallized from the mixture of *n*-hexane and toluene to give a white plate; yield 86.3 %, TLC (SiO₂, ethyl acetate : hexane = 1 : 3 v/v) R_f = 0.31; FT-IR (KBr) $\nu_{\text{C-H}}$ 2957, 2926 and 2865 cm⁻¹, $\nu_{\text{S-O}}$ 1193 and 1180 cm⁻¹, 834 and 813 cm⁻¹ (1,4-substituted benzene); ¹H-NMR (300 MHz, CDCl₃, TMS, 303 K), δ 0.89 (3H, t, CH₃), 1.19 (14H, s, (CH₂)₇), 2.46 (9H, s, ArCH₃), 3.76 (6H, s, CH₂OTs), 7.35 (6H, d, C-ArH), 7.71 (6H, d, S-ArH); GC-MS (EI) m/z M⁺680.1.

Synthesis of 1,1,1-tris (azidemethyl) nonane (3) [17]

Sodium azide (13.8 g, 212 mmol, 4.5 eq.) was added to the solution of **2** (31.8 g, 46.70 mmol) in diethylene glycol and stirred for 24 h at 408 K under N₂ flow. After cooling, the mixture solution was poured into ice water. Diethyl ether was added to the resulting solution to extract the product. The organic and aqueous layers were collected separately, and to extract the product a small portion of diethyl ether was added to the aqueous

solution. The operation was carried out more than four times. The organic solution was washed with 1 M hydrochloric acid, the saturated sodium chloride solution, and distilled water three and one time, respectively, and dried over anhydrous magnesium sulfate. After filtration, the organic solution was treated with activated charcoal to decolorize, and the solvent was evaporated. The residue was dried *in vacuo*; yellow oil; yield 90.6 %, TLC (SiO₂, chloroform : methanol = 20 : 1 v/v) $R_f = 0.80$; FT-IR (neat) ν_{C-H} 2957, 2926 and 2855 cm⁻¹, ν_{N_3} 2102 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃, TMS, 303 K), δ 0.88 (3H, t, CH₃), 1.26 (14H, s, (CH₂)₇), 3.27 (6H, s, CH₂N₃).

Synthesis of 1,1,1-tris (aminomethyl) nonane (4) [17]

The solution of **3** (5.03 g, 17.16 mmol) in dry-THF (20 cm³) was added dropwise (1 h) to the suspension of LiAlH₄ (4.17 g, 110 mmol, 6.4 eq.) in dry-THF in an ice bath under N₂ flow. After addition, the mixture was refluxed for 46 h. After cooling, distilled water (120 cm³) was added to deactivate the excess of LiAlH₄ in an ice bath, and the solution was stirred for 30 min. The resulting white solid was filtrated. After the filtration, the solvent was evaporated, and chloroform was added to extract the product. The solvent was evaporated and dried *in vacuo*; pale yellow oil; yield 91.6%, FT-IR (neat) ν_{N-H} 3373 and 3293 cm⁻¹ (primary amine), ν_{C-H} 2924 and 2854 cm⁻¹, γ_{N-H} 1600 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃, TMS, 303 K,) δ 0.88 (3H, t, CH₃), 1.23 (20H, s, (CH₂)₇ and NH₂), 2.58 (6H, s, CH₂NH₂).

Synthesis of broom methylcarbamoylmethoxy-acetic acid (5) [18]

Diglycolic anhydride (1.76 g, 15.13 mmol, 3.3 eq.) was added to solution of **4** (1.05 g, 4.88 mmol) in a mixture of dichloromethane (50 cm³) and THF (10 cm³) The mixture solution was stirred for 70 h at room temperature under N₂ flow. After stirring, distilled water (3 cm³) was added to decompose the excess of the anhydride and the solution was stirred overnight. The reaction solution was dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated, and then white crude viscous product was dried *in vacuo*. It was recrystallized from acetonitrile to give white crystals; yield 66.8 %; FT-IR (KBr) ν_{N-H} and ν_{O-H} 3327 cm⁻¹, $\nu_{C=O}$ 1635 cm⁻¹, γ_{C-O} 1140 cm⁻¹; ¹H-NMR (300 MHz, C₂D₆OS, TMS, 303 K,) δ 0.86 (3H, t, CH₃), 1.18 (14H, s, (CH₂)₇), 2.96 (6H, d, CH₂NHCO), 4.01 (6H, s, CH₂OCH₂), 4.13 (6H, s, CH₂OCH₂), 8.05 (3H, t, NHCO), 12.71 (3H, s, COOH).

Preparation of impregnated resin

Amberlite XAD-7 (purchased from Organo Co., Ltd.) was washed with methanol and distilled water, and dried *in vacuo*. The synthesized reagent (1.19 g) was dissolved in an analytical grade 1,4-dioxane (100 cm³). The dried XAD-7 (3.57 g) was immersed in the solution at a maximum

weight ratio of 1:3 (reagent: XAD-7) overnight. The solvent was completely evaporated; the obtained resin was dried *in vacuo*.

Adsorption tests of rare earth metal ions

Adsorption tests were carried out using the conventional batch method. Aqueous metal solutions were prepared by dissolving individual metal nitrate salts in 0.1 M hydrochloric acid or 0.1 M HEPES (2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulfonic acid) buffer solution to the concentration of 0.1 mM. Next, the solutions were arbitrarily mixed to adjust the pH. 0.02 g of the impregnated resin was added to 10 cm³ of the solution and the mixture was shaken at 303 K for more than 15 h. After filtration, the metal concentration and the pH of the aqueous solutions were measured with an ICP-AES (Shimadzu, ICPS-5000) and a pH meter (Orion, φ720A), respectively.

RESULTS AND DISCUSSION

Adsorption tests of rare earth metal ions

The time necessary to reach adsorption equilibrium was evaluated by changing shaking time during adsorption tests. The influence of shaking time on the percentage adsorption of La, Pr and Nd is shown in Fig.4. The percentage adsorption, %A, is defined by equation (1),

$$\%A = \frac{C_{ini.} - C_{eq.}}{C_{ini.}} \times 100 \quad (1)$$

where $C_{ini.}$ and $C_{eq.}$ represent the initial and the equilibrium rare earth metal concentrations in the aqueous solution, respectively.

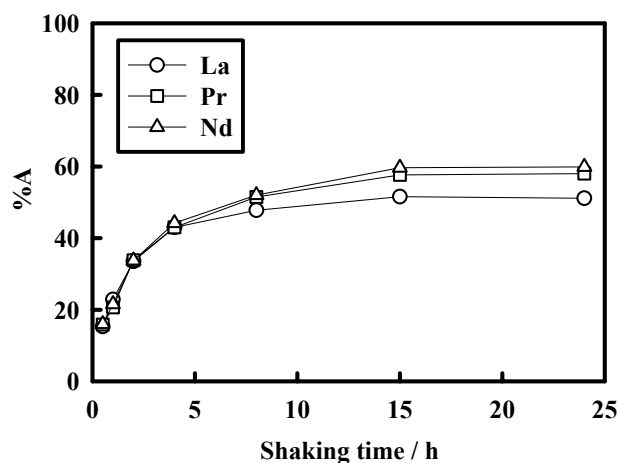


Fig. 4. Effect of shaking time on the percentage adsorption of La, Pr and Nd. Weight of resin: 0.02 g, 0.1 M HCl-0.1 M HEPES, initial pH = 5.0.

The adsorption of metal ions reached equilibrium within 15 h. It was reported that the adsorption rate is affected by wetting of resin [15]. Amberlite XAD-7 is a hydrophobic macroporous resin, in which the aqueous solution permeates with difficulty. The ion-exchange rate between the reagent and the metal during adsorption can be sufficiently fast. The slow rate may be attributed to the fact that the surface of the resin was not rendered hydrophilic, or to the diffusional resistance.

The influence of pH on the percentage adsorption, %A, of nine rare earth metal ions is shown in Fig. 5. The XAD-7 resin (with ester group only) exhibits just poor adsorption of rare earth metal ions in pH ranging from 2 to 5, responsible for physical adsorption. For all rare earth metal ions employed, pH dependence on the percentage adsorption was observed, which shows that the metal adsorption occurs according to cation-exchange mechanism between carboxyl groups and metal ions. However, since the percentage adsorption reaches plateau at approximately 70%, it seems that the interaction between the reagent and the ester group of XAD-7 is stronger than that between metal species and the reagent in high pH range.

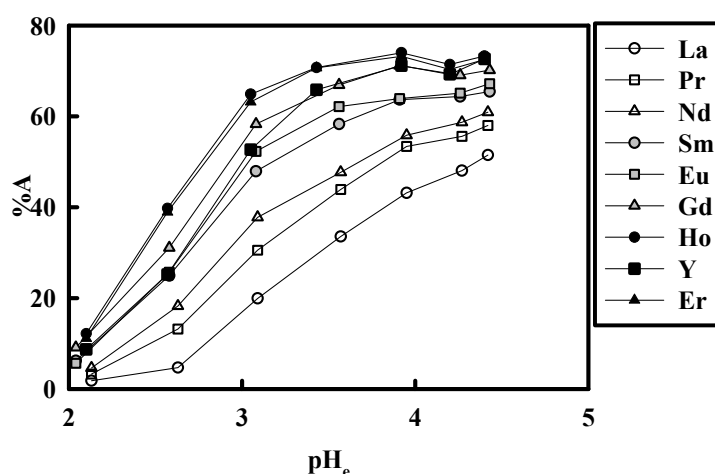


Fig. 5. Effect of pH on percentage adsorption of rare earth metal ions.
Weight of resin: 0.02 g, 0.1 M HCl – 0.1 M HEPES.

Apparently, the adsorption selectivity towards heavy rare earths appears, and the selectivity order is as follows: Ho>Er>Gd>Y>Eu>Sm>>Nd>Pr>>La. This order is almost completely different from those of general carboxylic acid extractants described by Preez et al. [19]. The $pH_{0.5}$ values, which correspond with 50% adsorption, toward rare earth metals are listed in Table 1. The relation between $pH_{0.5}$ and reciprocal numbers of the ionic radii of rare earths (in hexa-coordination) is shown in Fig.6. From Table 1 and Fig.6, group separation (between light and middle rare earths) is easy by

using the present resin, and mutual separation within the group could be achieved. The present resin also shows selectivity towards holmium and erbium rather than towards light rare earths.

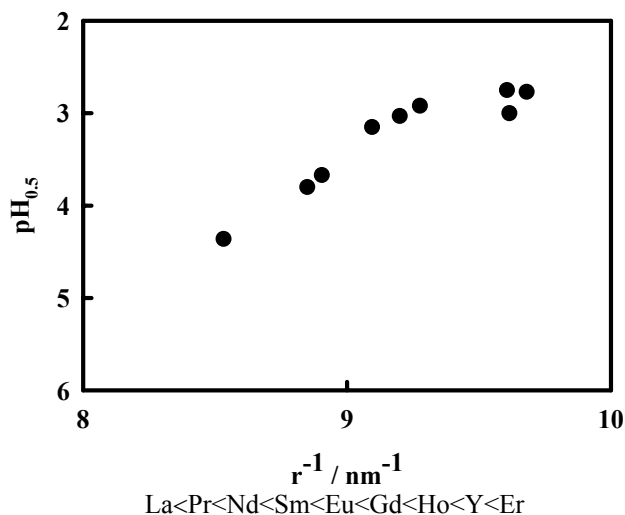


Fig. 6. Relation between the $\text{pH}_{0.5}$ values and reciprocal numbers of the ionic radii of rare earths.

Table 1. The $\text{pH}_{0.5}$ value for each the rare earth for the present resin

RE	$r^{-1} (\text{nm}^{-1})$	$\text{pH}_{0.5}$
La	8.53	4.36
Pr	8.85	3.80
Nd	8.90	3.67
Sm	9.11	3.15
Eu	9.20	3.03
Gd	9.28	2.92
Ho	9.61	2.75
Y	9.62	3.00
Er	9.68	2.77

It is suggested that the structural effect of the tripodal broom molecule with a narrow coordination site stimulates the selectivity towards smaller heavy rare earths cations.

The maximum loading capacity for holmium ions on the present resin is shown in Fig.7, where adsorbed amount, q (mol kg^{-1}), is defined by equation (2).

$$q = \frac{C_{\text{ini.}} - C_{\text{eq.}}}{w} \times V \quad (2)$$

w and V represent the amount of resin (kg) and volume of an aqueous solution (dm^3), respectively.

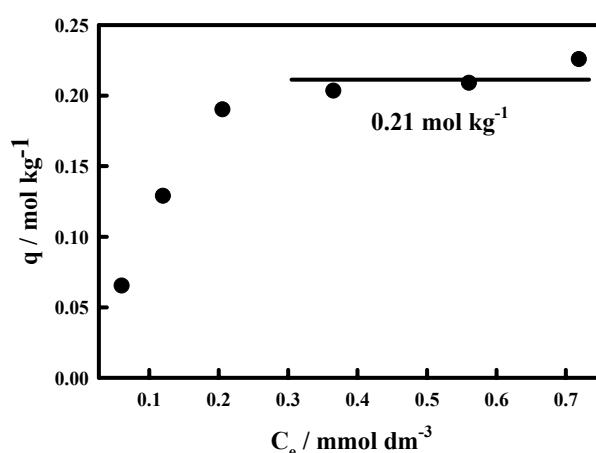


Fig. 7. Maximum loading capacity of the present resin for holmium. Weight of resin: 0.02 g, volume of the solution: 10 cm^3 , initial pH = 3.9.

The amount of holmium adsorption increases with increasing metal concentration and reaches the constant value of 0.21 mol kg^{-1} corresponding with the maximum adsorption capacity of the impregnated resin. Langmuir plot for holmium on the present resin was drawn to confirm. In the figure, plots lie on straight line with a slope of 4.15. From Langmuir isotherm equation, the theoretical maximum loading capacity is 0.24 mol kg^{-1} , which well corresponds with the experimental results. The content of the impregnated reagent was 25 wt %, which is equal to 0.44 mol kg^{-1} . A comparison of the both values suggests that stoichiometry in the resin is 1:2 (holmium : reagent). The maximum loading capacity of holmium depends on the stoichiometry of the complex between the impregnated reagent and metal ion. Although the structure of complex between the broom molecule and metal ions is not recognized, when one metal ion and two molecules form a sandwich type complex, two hard oxygen atoms of carbonyl and one

ether in functional groups will participate in coordination with metal ions to form a stable five-membered chelate ring. The examination with spectroscopic methods is required for detailed elucidation of the complex structure.

CONCLUSIONS

The tripodal broom methylcarbamoylethoxy-acetic acid impregnated resin has been prepared to investigate the adsorption behavior of rare earth metal ions. It is the first report on an ion-exchanger containing broom compound with adsorption ability for rare earth metal ions, and selectivity towards smaller heavy rare earths cations. The novel tripodal broom molecule exhibits high potential as a reagent for the separation of rare earth metals.

REFERENCES

- [1] E. Shchori, J.J. Grodzinski, *J. Appl. Polym. Sci.*, 1976, 20 (3), 773-788.
- [2] M. Cinouini, S. Colonna, H. Molinari, F. Montanari, P. Tundo, *J. Chem. Soc., Chem. Commun.*, 1976, (11), 394-396.
- [3] K. Ohto, Y. Senba, N. Eguchi, T. Shinohara, K. Inoue, *Solv. Extr. Res. Dev., Jpn.*, 1999, 6, 101-112.
- [4] Y. Wakui, H. Matsunaga, T.M. Suzuki, *Anal. Sci.*, 1988, 4, 325.
- [5] J. Shibata, S. Matsumoto, H. Yamamoto, *Solv. Extr. Res. Dev., Jpn.*, 2000, 7, 167-175.
- [6] W.J. Kasowski, J.C. Bailar, Jr., *J. Am. Chem. Soc.*, 1969, 91, 3212-3218.
- [7] R. McCrindle, A.J. McAless, *J. Chem. Soc., Perkin*, 1981, 741-745.
- [8] R. Viguier, G. Serratrice, A. Dupraz, C. Duppy, *Eur. J. Inorg. Chem.*, 2001, 1789-1795.
- [9] R. Katakay, D. Parker, A. Teasdale, *Anal. Chim. Acta*, 1993, 276, 353-360.
- [10] H.J. Lu, Y.T. Fan, Y.J. Wu, M.C. Yin, *Polyhedron*, 2001, 20, 3281-3286.
- [11] M.M. Meijler, R.A. Yellin, Z. loav Cabantchik, A. Shanzer, *J. Am. Chem. Soc.*, 2002, 124, 12666-12667.
- [12] J.S. Li, Y.Y. Chen, X.R. Lu, *Eur. J. Org. Chem.*, 2000, 485-490.
- [13] M.M. Reinoso-Garcia, A. Dijkman, W. Verboom, D.N. Reinhoudt, E. Malinowska, D. Wojciechowska, M. Pietrzak, P. Selucky, *Eur. J. Org. Chem.*, 2005, 2131-2138.
- [14] G. Zuijun, N. Yanning, Z. Weiguang, T. Minyu, *J. Radioanal. Nucl. Chem.*, 2003, 262(2), 331-337.
- [15] K. Ohto, H. Nakagawa, H. Furutsuka, T. Shinohara, T. Nakamura, T. Oshima, K. Inoue, *Solv. Extr. Res. Dev., Jpn.*, 2004, 11, 121-134.
- [16] O.C. Demer, P.W. Solomon, *J. Am. Chem. Soc.*, 1954, 76, 1697-1699.
- [17] E.B. Fleischer, A.E. Gebala, A. Levey, P.A. Tasker, *J. Org. Chem.*, 1971, 36, 3042-3044.
- [18] J.W. Lee, J.Y. Lu, P.S. Low, P.L. Fuchs, *Bioorg. Med. Chem.*, 2002, 10, 2397-2414.
- [19] A.C. du Preez, J.S. Preston, *Solv. Extr. Ion. Exch.*, 1992, 10 (2), 207-230.