



EXTRACTION MECHANISM OF LEAD ION WITH *p*-ALLYLCALIX[4]ARENE TETRACARBOXYLIC ACID

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ABSTRACT

25,26,27,28-Tetrakis(carboxymethoxy)-5,11,17,23-tetraallylcalix[4]arene in a cone conformation has been synthesized for the selective extraction of divalent lead ions. The extraction of divalent metal ions, such as lead, copper, nickel and zinc with *p*-allylcalix[4]arene tetracarboxylic acid was investigated. The extraction data and chemical shift of ¹H-NMR for the extractant, caused by the complexation with lead, supports the conclusion that two lead ions are extracted stepwise. The complex structure was proposed.

Keywords: *p*-allylcalix[4]arene tetracarboxylic acid, Extraction, Selectivity, Lead, Peak shift

INTRODUCTION

Calixarenes are cyclic oligomers and the third group host compound with properties discriminating some specific metal ions and organic compounds. A number of studies properties of calixarenes has been carried out and their specific behavior has been reviewed [1,2]. The authors have

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focused on the use of calixarene compounds as solvent extraction reagents for metal ions separation. In our previous works, the specific extraction behavior has been reported [3-9]. Among them, their ability to selective lead extraction is one of the remarkable properties for calixarene derivatives. It is attributed to effect of the size fitting and the presence of functional groups [7].

In this work, *p*-allylcalix[4]arene tetracarboxylic acid derivative in the cone conformation has been prepared to investigate the extraction of divalent metal ions such as lead, copper, zinc, and nickel. In the case of lead extraction, proton nuclear magnetic resonance study has also been carried out to elucidate the lead extraction mechanism.

MATERIALS/METHODS/PROCEDURES

Reagents

5,11,17,23-Tetra-*t*-butylcalix[4]arene-25,26,27,28-tetrol and debutylated calix[4]arene-25,26,27,28-tetrol were synthesized in a manner similar to those described by Gutsche et al. [10,11]. 25,26,27,28-Tetraallyloxycalix[4]arene and Claisen-rearranged 5,11,17,23-tetraallylcalix[4]arene-25,26,27,28-tetrol (compound **1**) were synthesized in a manner similar to those described by Iwamoto *et al.* [12] and Gutsche et al. [13].

25,26,27,28-Tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetraallylcalyx[4]arene (**2**) (cone conformation) and 25,26,27,28-tetrakis(carboxymethoxy)-5,11,17,23-tetraallylcalix[4]arene (**3**) (cone conformation) were synthesized in a manner similar to that described in the previous paper [3]. The synthetic scheme of the present extractant, **3**, is shown in Fig.2.

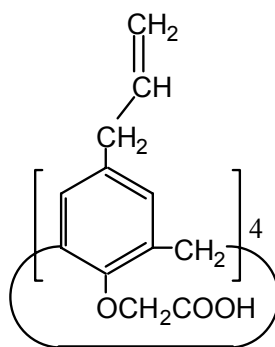


Fig. 1. Chemical structure of the present extractant.

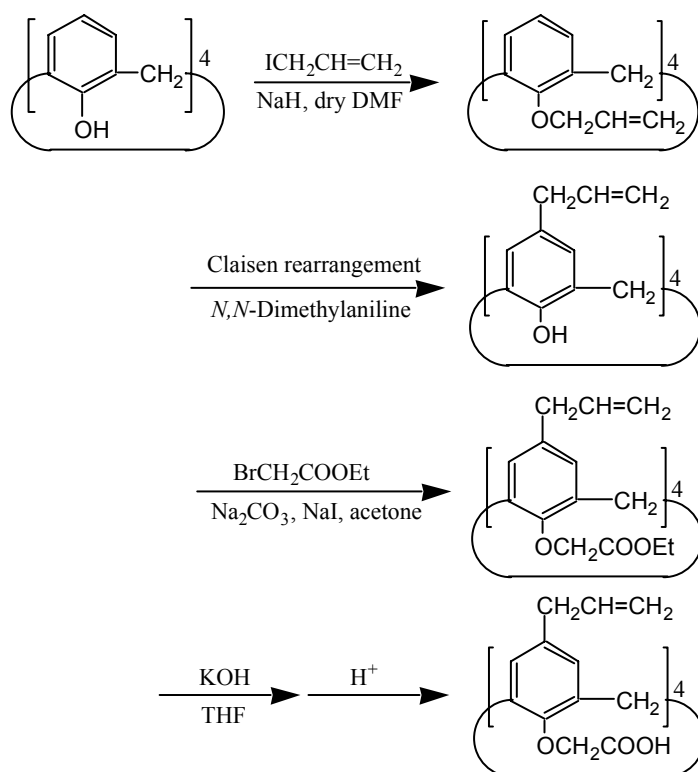


Fig.2. Synthetic scheme of the present extractant.

25,26,27,28-Tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetraallyl calix[4]arene (2) (cone conformation)

Compound 1 (6.40 g, 10.9 mmol), sodium iodide (26.1 g, 174 mmol) and sodium carbonate (23.1 g, 218 mmol) were added under the N_2 atmosphere, to 300 cm^3 of dry acetone. The solution was stirred for a half hour and to the solution ethyl bromoacetate (29.1 g, 174 mmol) was added. The solution was refluxed for 28 h. After cooling, the excess of sodium carbonate was filtered off, the solvent was removed *in vacuo*. The residue was dissolved in chloroform. The organic layer was washed with 1 M HCl and distilled water, and then dried over anhydrous MgSO_4 . After the filtration, the solvent and excess of ethyl bromoacetate was removed *in vacuo*. The recrystallization was carried out from ethanol.; on Pale yellow powder, 6.54 g (64.6%), TLC (SiO_2 , chloroform : methanol = 5:1 v/v, $R_f = 0.40$); IR (KBr) disappeared peak $\nu_{\text{O-H}} 3150 \text{ cm}^{-1}$, $\nu_{\text{C=O}} 1757 \text{ cm}^{-1}$; $^1\text{H NMR}$ (300 MHz, CDCl_3 , TMS, 30°C) δ 1.28 (12H,t, CH_2CH_3), 3.06 (8H,d, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.15 (4H,d,Ar- CH_2 -Ar(*exo*)), 4.20 (8H,q, CH_2CH_3), 4.72 (8H,s, OCH_2COO), 4.84 (4H,d,Ar- CH_2 -Ar(*endo*)), 4.94 (8H,m, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.79 (4H,m, $\text{CH}_2\text{CH}=\text{CH}_2$), 6.49 (8H,s,ArH).

25,26,27,28-Tetrakis(carboxymethoxy)-5,11,17,23-tetraallylcalyx[4] arene (3) (cone conformation).

2 (6.50 g, 7.00 mmol) and KOH (7.07 g, 126 mmol) in 200 cm³ of water were added to 300 cm³ of tetrahydrofuran. The mixture was refluxed for 70 h. After cooling, to the mixture was added 50 cm³ of 6 M HCl in an ice bath. To the mixture chloroform was added to extract the desired compound. The mixed organic layer was washed with 1M HCl and distilled water, and then dried over anhydrous MgSO₄. After the filtration, the solvent was removed *in vacuo*. The reprecipitation was carried out from hexane; brown powder, 4.27 g (74.7%), TLC (SiO₂, chloroform : methanol = 5:1 v/v, $R_f = 0.49$); IR (KBr) ν_{COOH} (br) 2500-3300 cm⁻¹; $\nu_{\text{C=O}}$ 1741 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS, 30°C) δ 3.11 (12H, d+s, CH₂CH=CH₂ + Ar-CH₂-Ar(*exo*)), 4.79 (20H, d+d+s, Ar-CH₂-Ar(*endo*)+ CH₂CH=CH₂ + OCH₂COO), 5.77 (4H, m, CH₂CH=CH₂), 6.67 (8H, s, ArH).

Distribution study

The extraction of metal ions was carried out according to the conventional batch-wise method [12]. Organic solutions were prepared by diluting the extractant into an analytical grade of chloroform to 5 mM. Aqueous solutions were prepared by dissolving metal chloride or nitrate salts in 0.1 M hydrochloric acid or 0.1 M HEPES (2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid) buffer solution to a concentration of 0.1 mM. Equal volumes (5 cm³) of both phases were mixed in an Erlenmeyer flask with a stopper and shaken at 303 K for several hours. After phase separation, the pH and the metal concentration of the aqueous solutions were measured by a pH meter (Beckman, ϕ 45) and an atomic absorption spectrophotometer (abbreviated as AAS, Shimadzu, AA-6650), respectively.

Proton nuclear magnetic resonance study of lead complexes

Organic solutions were prepared by diluting the extractant with an analytical grade CDCl₃ to a concentration of 5 mM. Aqueous solutions were prepared by dissolving lead nitrate salts into 0.1 M HEPES D₂O solution to 5 mM. (The pH value was adjusted by 6 M HCl.) Both phases (phase ratio = 3:1, aqueous:organic) were mixed in an Erlenmeyer flask with a stopper and shaken at 303 K for several hours. After phase separation, the peaks and the integral ratios of the extractant in the organic phase were recorded by a proton nuclear magnetic resonance spectrometer (Jeol, JNM-GX270). The lead concentrations in the aqueous phase were also determined by AAS.

RESULTS AND DISCUSSION

Distribution study

Time required to reach equilibrium for lead extraction has been examined. Effect of shaking time on the extraction of lead ion is shown in Fig.3. The extractability, %E, is defined by equation (1)

$$\% E = \frac{[\text{Pb(II)}]_{\text{org}}}{[\text{Pb(II)}]_{\text{ini}}} \times 100 \quad (1)$$

where $[\text{Pb(II)}]_{\text{org}}$ and $[\text{Pb(II)}]_{\text{ini}}$ represent the extracted and the initial lead concentrations, respectively. Extraction of lead ion with the extractant is sufficiently fast and reaches equilibrium within 2 h.

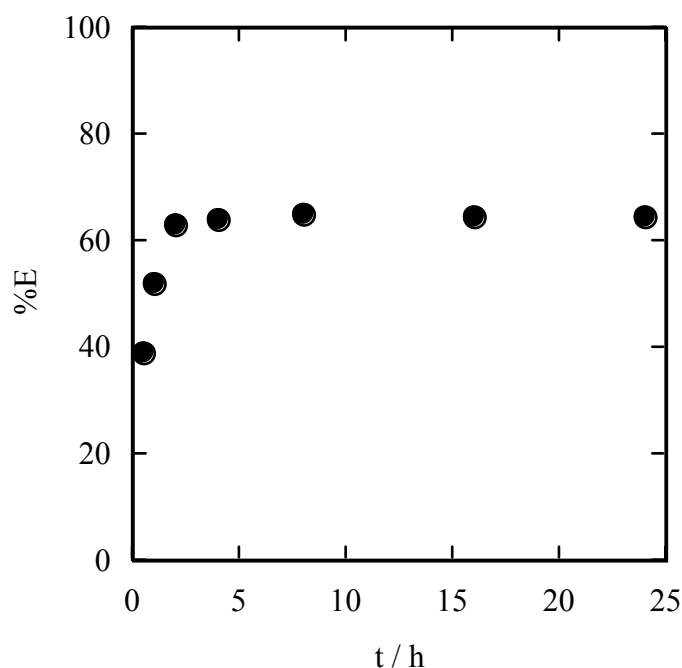


Fig.3. Effect of shaking time on percentage extraction of lead.
 $[\text{Pb}^{2+}] = 0.1 \text{ mmol dm}^{-3}$, initial pH = 1.93.

The effect of pH on distribution ratio, D , of metal ions, Pb(II), Cu(II), Zn(II), and Ni(II) is shown in Fig.4. All the plots lie on straight lines at slopes of 2 as expected from metal charges. All metal ions are just ion-exchanged with the present extractant during the extraction. The order of selectivity to metal ions for the present extractant is similar to that of *p*-*t*-octylcalix[4]arene tetracarboxylic acid, i. e.: $\text{Pb} \gg \text{Cu} > \text{Zn} > \text{Ni}$ [10]. These orders are also similar to those of common carboxylic acid type of the extractants. Calix[4]arene carboxylic acid type of the extractants, however, show the specific high selectivity for the lead ions in the presence of other divalent metal ions.

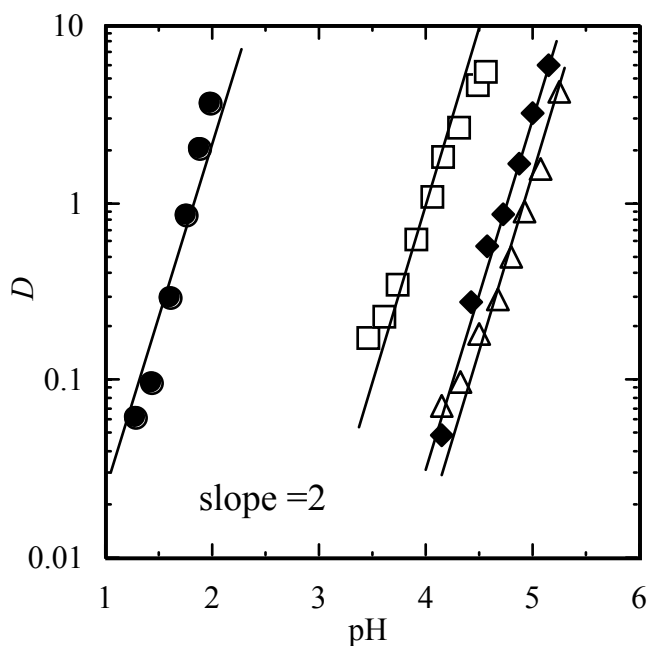


Fig. 4. Effect of equilibrium pH on distribution ratio of divalent metals.
 ● Pb(II), □ Cu(II), ◆ Zn(II), △ Ni(II), [Metal]=0.1 mmol dm⁻³,
 [Extractant] = 5 mmol dm⁻³, 0.1 mol dm⁻³ HCl - 0.1 mol dm⁻³ HEPES.

The pH region of lead extraction significantly shifts to its lower values, contrary to our expectation based on the stability constants of divalent lead ion and acetic acid compounds (those of other divalent metal extractions are as expected). It is obvious that the structural contribution of the cyclic tetrameric extractant involves in the selectivity enhancement of lead only, which seems to be attributable to the size-fitting of the coordination site consisting of four functional groups in the cyclic tetrameric compound for the lead ion described in the previous work [7].

Proton nuclear magnetic resonance study of lead complex

In order to confirm the stoichiometry of the lead extraction reaction and elucidate the extraction mechanism, proton nuclear magnetic resonance study of lead complex has been carried out. Figure 5 shows the partial spectra of the present extractant after lead extraction at various pH values together with the shifted percentage of aryl peak and the loading percentage of lead on the extractant calculated from chemical analysis of AAS.

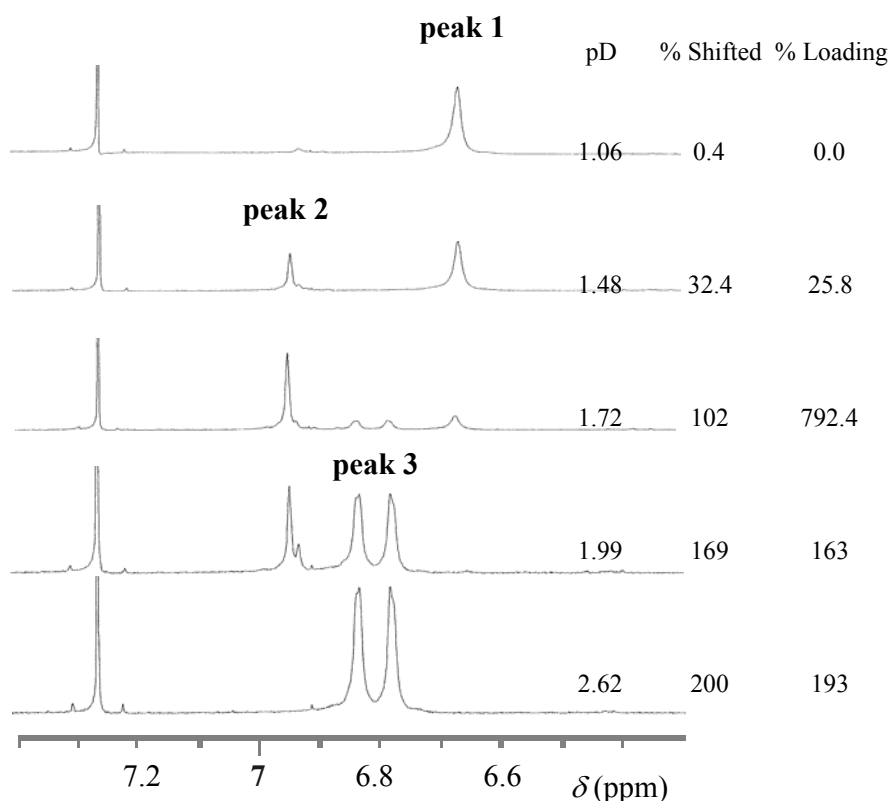


Fig. 5. Partial ^1H -NMR spectra of the extractant **1** at various pHs after extraction together with the shifted percentage of aryl peak and the loading percentage of lead on the extractant calculated from chemical analysis of AAS.

The chemical shift of the original peak was observed in the spectra with increasing pH. A further shift was also observed at higher pH value. That is, as shown in Fig.5 the aryl peak of free extractant appears at 6.70 ppm (**peak 1**) and the original peak shifts to 6.97 ppm (**peak 2**) step by step with an increase of the pH value. After the original peak disappears and new shifted peak becomes major almost, the further peaks appear as doublet at 6.83 ppm (**peak 3**). Finally those peaks are only observed. From the present and previous [10] results, the shifted degree of the peak and the loading percentage of lead would be closely correlated. The percentage of chemical shift was calculated from the integral ratio of aryl protons based on the eq.(2) and (3). For the first shift at pH values lower than 1.7, the shifted percentage is defined by the eq.(2).

$$\% \text{shifted} = \frac{2}{1+2} \times 100 \quad (2)$$

For the second shift at pH higher than 1.7, the shifted percentage is defined by eq.(3).

$$\% \text{shifted} = \frac{(2+3)+3}{2+3} \times 100 \quad (3)$$

where **1**, **2**, and **3** represent the integral ratios of the **peaks 1**, **2**, and **3**.

Since the second shift seems to take place stepwise after the extraction of the first lead, the third doublet peaks (at the second shift) is counted twice.

The effects of pD on the percentage shifted of aryl peak in the extractant (evaluated from eq.(2) and (3) by means of $^1\text{H-NMR}$ spectrometry) The percentage loading of lead on the extractant (evaluated from the chemical analysis by means of atomic absorption spectrometry) are shown in Fig.6. Both values are independent, as evaluated from the different measurements. Both plots, however, agree well with each other and the good correlation between the percentage shifted and the percentage loading is observed. The both percentages increase with the increase of pD and finally reach 200%. The second chemical shift was observed after the complete shift from the original one. From these results, it is assumed that the second lead ion is stepwise extracted after the complete loading of the first lead on the extractant.

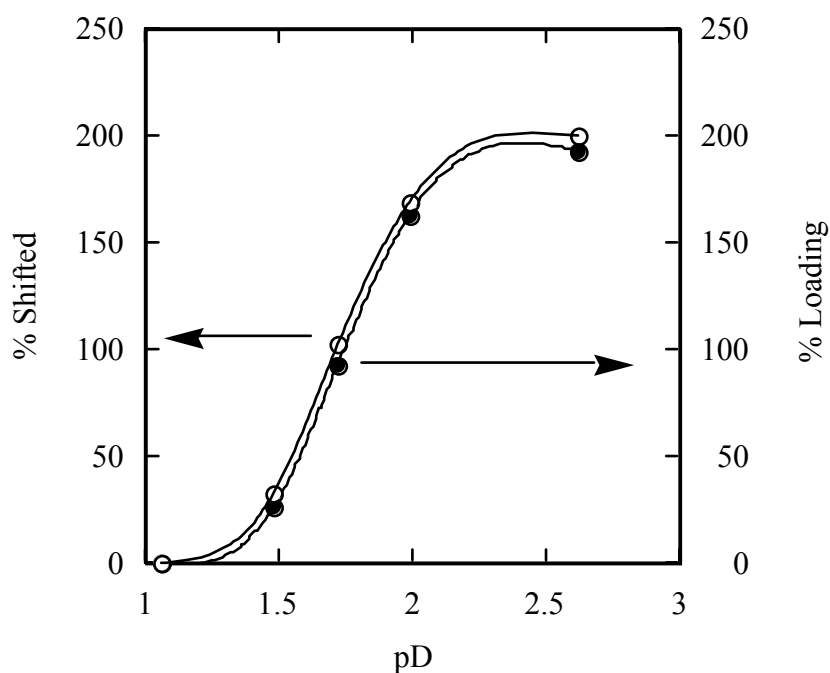


Fig.6. Effect of pD on percentage loading of lead and percentage shifted of the present extractant. $[\text{Pb}^{2+}] = 5 \text{ mmol dm}^{-3}$ in D_2O , $[\text{Extractant}] = 5 \text{ mmol dm}^{-3}$ in CDCl_3 , $\text{CDCl}_3:\text{D}_2\text{O} = 1:3$ (v:v), \circ % shifted, \bullet % shifted.

Here, the peaks in Fig.5 are focused again. The original **peak 1** is singlet, the first shifted **peak 2** is also singlet, and the second shifted **peaks 3** are doublet. The original **peak 1** is equivalent and singlet. The **peak 2** must be equivalent, whereas the peaks 3 would not be equivalent and there are two environmentally different peaks. Thus, the coordination site for the first lead ion would consist of phenoxy oxygens and carbonyl oxygens for the coordination, and two carboxyl groups for the ion-exchange. In the step, two carboxyl groups are easily changeable to the rest two groups and the exchange rate would be faster than the measurement speed of $^1\text{H-NMR}$. Consequently, the aryl peak would be equivalent and singlet. On the contrary, the coordination site for the second lead ion would be C_2 symmetric, which appears as doublet peaks. Thus, at the second step, the coordination is significantly tight and the functional groups are almost fixed after the lead extraction. In the step, two carboxyl groups at distal position would bind with the first lead and the rest two groups at distal position would bind the second lead. That is, two lead ions are also taken up at the inside of the coordination site of the extractant and vertically alongside each other of the phenoxy rings. The proposal structure is shown in Fig.7.

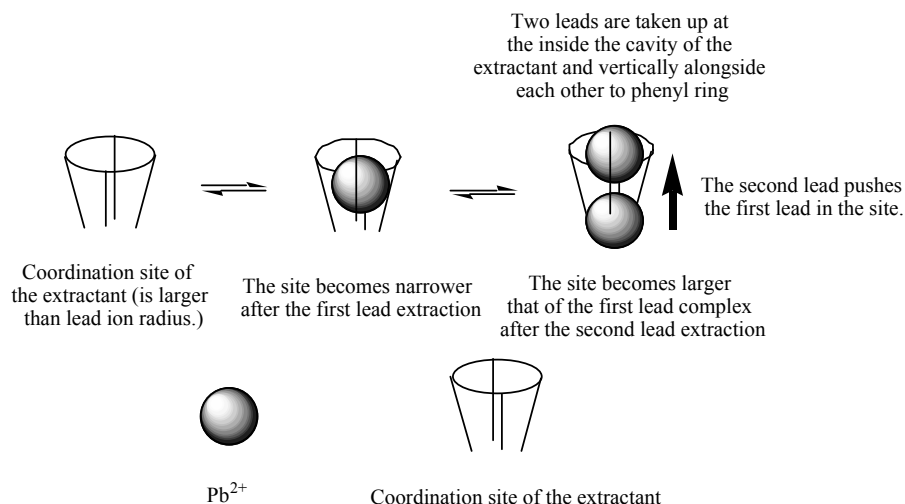


Fig.7. Proposed structure of the lead complex for the extractant.

The structure is the most conceivable form expected from $^1\text{H-NMR}$ spectra after the complexation. The detailed consideration is given. Since the size of the coordination site in the free extractant is larger than that of diameter for lead ion, it must become narrower after the first lead extraction. Consequently, the opposite aryl protons from the coordination site is far

from each other compared with those in the free extractant and the peak shifts to a lower magnetic field. On the other hand, in the second lead extraction, the second lead ion would push the first lead in the coordination site due to the steric hindrance of two lead ions. It causes the expansion of phenoxy oxygens, in consequence the doublet peaks shift to a higher field.

CONCLUSION

Tetracarboxylic acid derivative of calix[4]arene with allyl radical has been prepared to investigate extraction behavior of various divalent metal ions. The present extractant shows high lead selectivity among divalent metal ions examined. Proton nuclear magnetic resonance study of lead complex has been also carried out. The results show that both the degrees of the chemical shift of the extractant peak and the lead loading on the extractant are closely correlated. It is proposed that two lead ions are vertically alongside extracted with a single molecule of the extractant.

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