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Liquid–Liquid Extraction of Transition and Alkali Metal Cations by a New Calixarene: Diphenylphosphino Calix[4]arene Methyl Ether

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Abstract. The liquid–liquid extraction of various metal ions by a diphenylphosphino calix[4]arene (**1**) using picrate counter ion has been studied and compared with those of *p*-*tert*-butyl-calix[4]arene methyl ether (**2**) and triphenylphosphine (**3**). The calixarene **1** shows strong binding ability to almost all metal cations examined, but calixarene **2** shows little ability to extract any of them. Based on the continuous variation method, calixarene **1** formed 1 : 2 complexes with copper(II) ion.

Key words. Calix[4]arene, solvent extraction, alkali metal ion, transition metal ion.

1. Introduction

The class of flexible macrocyclic hosts known as calixarenes has recently received increasing attention [1, 2]. Calixarenes are composed of benzene moieties whose functionalization of the upper rim of the calix, R (Figure 1), can be expected to improve or alter their inclusion properties [3–7]. One of the more interesting aspects of our work has been the preparation of new calixarenes with a view to complexing transition metals, an area which has been slow to develop [8–11].

Here we report the synthesis and ion binding properties of a new calixarene having the diphenylphosphino moiety at the upper rim of the calix.

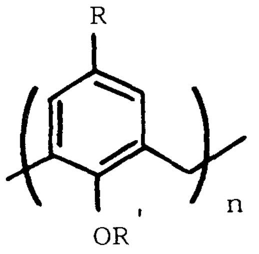

Fig. 1. Schematic structure of a calix[*n*]arenes.

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2. Experimental

2.1. PREPARATION OF DIPHENYLPHOSPHINO CALIX[4]ARENE METHYL ETHER

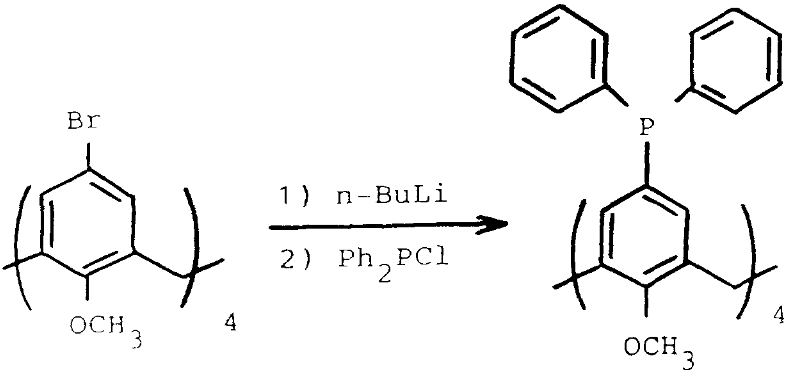
To a solution of 4.80 g (6.03 mmol) of bromocalix[4]arene methyl ether [7] in 300 mL of dry THF cooled to −78°C under a nitrogen atmosphere was added 16.60 mL (26.53 mmol) of *n*-butyl lithium (15% in hexane). The reaction mixture was maintained at −78°C for an additional hour. A solution of Ph_2PCl (5.85 g, 26.53 mmol) in 10 mL of dry THF was added dropwise and the mixture was warmed to room temperature and stirred for one hour. The reaction mixture was evaporated off and the residue was chromatographed on silica gel using *n*-hexane–acetone as an eluting solvent. The *n*-hexane–acetone (10 : 1) eluted fractions were collected and evaporated off to give a white powder. Recrystallization from $CHCl_3$–MeOH afforded the product (4.45 g, 58.63%) as a white powder: m.p. 113.5–114.6°C, IR(KBr) 3080, 3060, 3000, 2860, 1590, 1480, 1440, 1260, 1220, 1090, 1030, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) = 2.8–4.1 (m, 20H, $ArCH_2Ar$ and OCH_3), 6.4–7.6 (m, 48H, ArH), Found: C, 75.31; H, 5.48. Calcd. for $C_{80}H_{68}O_4P_4 \cdot 3H_2O$: C, 75.58; H, 5.87.

2.2. EXTRACTION PROCEDURE

A chloroform solution (10 mL) of ligand (1×10^{-3} mol dm^{-3}) and an aqueous solution (10 mL) containing 2×10^{-5} mol dm^{-3} of picric acid and 1×10^{-2} mol dm^{-3} of metal nitrate were stirred at 25° for 24 h. An aliquot of the upper aqueous solution was withdrawn, and the UV spectrum was recorded. A similar extraction was performed without ligand. The extractability was determined on the basis of the absorbance of picrate ion in the aqueous solutions by means of the following equation:

$$\text{Extractability}(\%) = [(A_0 - A)/A_0] \times 100$$

where A_0 is the absorbance in the absence of the ligand.



Scheme 1.

3. Results and Discussion

The synthesis of **1** is shown in Scheme 1. *p-tert*-Butyl calix[4]arene methyl ether (**2**) was synthesized according to Gutsche's method [12]. The ^{1}H-NMR of **1** displays a very complicated pattern which suggests **1** may exist in different configurations in solution [13]. Although the UV spectrum of **1** shows no absorption above 300 nm, a new absorption over 400 nm is found when copper ion is added to **1** in THF solution (Figure 2).

This is interpreted to mean that **1** and Cu^{2+} are complexed in solution. We determined the ratio of **1** and copper ion in the complex by the continuous variation plots method [14]. As illustrated in Figure 3, the compound of **1** and Cu^{2+} has its maximum absorbance at $[(Cu(NO_3)_2)/(calix + Cu(NO_3)_2)] = 0.65$. The results shows that **1** forms a 1 : 2 complex with Cu^{2+} in solution.

Calix[4]arene can adopt four extreme geometries, which have been designated as 'cone', 'partial-cone', '1,2-alternate', and '1,3-alternate' conformations [13]. Although most of the inclusion and cation complexation chemistry is based on the cone configuration, the present 1 : 2 complex may have the 1,3-alternate conformation as shown in Figure 4, in which steric repulsion between the diphenylphosphino moieties should be the smallest of these four conformations.

In order to compare the complexation characteristics of the ligands (**1**, **2**, and **3**), the solvent extraction of several metal cations with picrate ion by these ligands was carried out in a water/chloroform system [15]. The results on the extraction of metal picrates with ligand are summarized in Table I. As shown in Table I, **1** exhibited enhanced extraction efficiency compared with **2** and **3**. The extractability of **1** for Cu^{2+}, Ni^{2+}, Hg^+, Cd^{2+} and Zn^{2+} cations was higher than for K^+, Na^+ and Al^{3+} cations. This phenomenon can be explained by the hard-soft acid-base principle; R_3P (R = phenyl in the present system) is a soft base and has stronger affinity

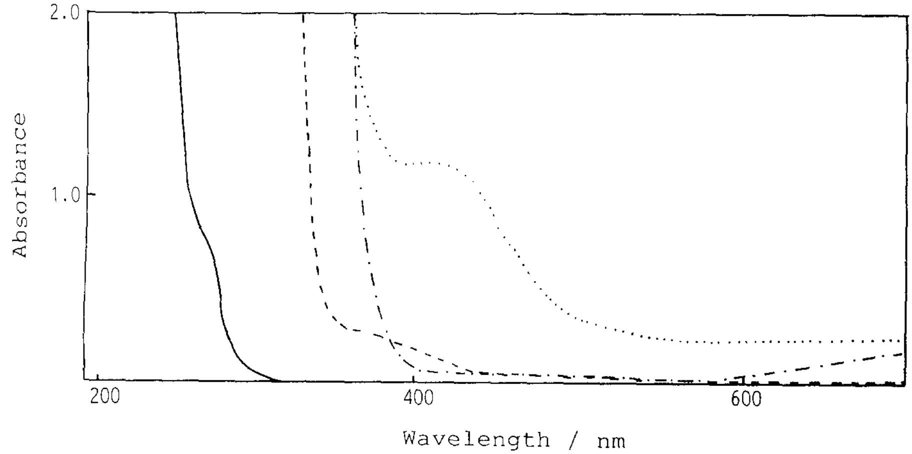


Fig. 2. The UV-visible absorption of a mixture of **1** and Cu^{2+} ion in different ratios of concentration. ——: 9.79×10^{-5}M of **1** in THF. - - -: 9.79×10^{-2}M of $Cu(NO_3)_2$ in THF. – · – · –: a mixture of **1** (6.853×10^{-3}M) and $Cu(NO_3)_2$ (2.937×10^{-3}M) in THF. · · · ·: a mixture of **1** (3.4265×10^{-3}M) and $Cu(NO_3)_2$ (6.363×10^{-3}M) in THF.

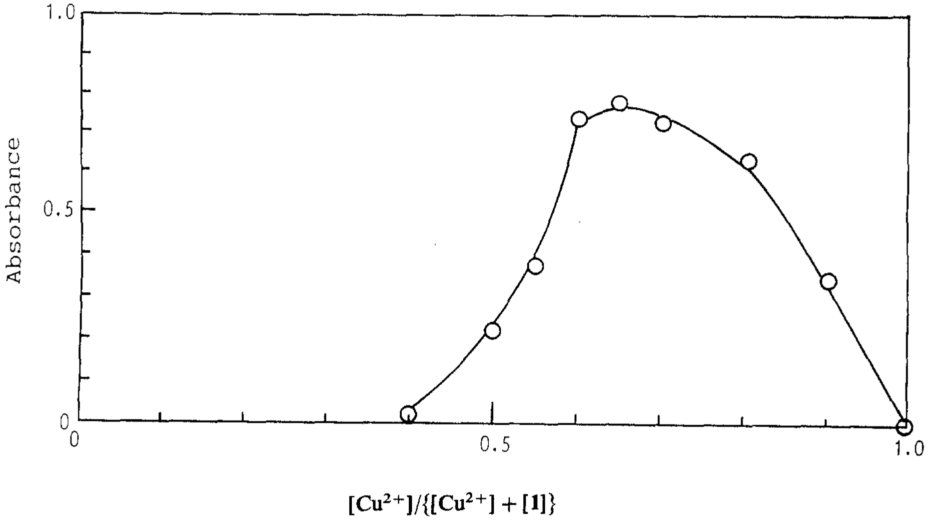


Fig. 3. Continuous variation plots for the formation of the Cu^{2+} complex: 25°C. [1] + [Cu(NO$_3$)$_2$] = 9.79 × 10^{-3}M.

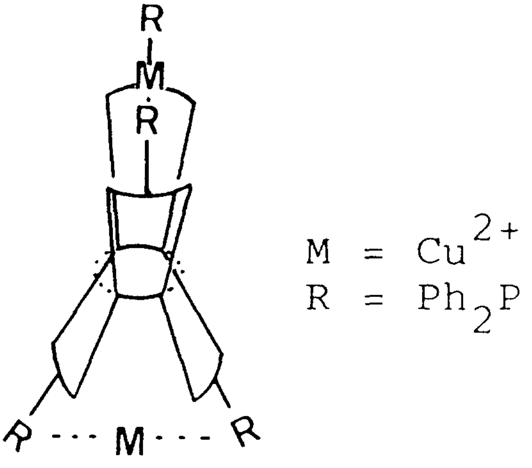


Fig. 4. 1,3-alternate configuration for calix(4)arene.

toward soft basic metal cations than hard metal cations. The strong participation of the R$_3$P group in the complexation in the present case was further confirmed by the results of extraction experiments with **2**. Although **2** has phenolic ether oxygen atoms, which are well known to be good ligands as reported by Atwood and co-workers [16], **2** shows little extractability to not only main group metal cations but also transition metals cations. When the extractability of **1** and **3**, which have the same binding site structure, is compared, **1** shows a much stronger ability to complex metal cations than does **3**. To our surprise, however, **3** does not show high extractability of metal cations except for Hg$^+$ in the present system in spite of the fact that many examples of the complexation of **3** and metal cations, especially for

Table 1. Extraction of metal picrates with ligands.

Ligand	Picrate salt extracted (%)							
	Na^+	K^+	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Hg^+	Al^{3+}
1	40	33	44	59	56	58	78	43
2	4	0	0	0	0	0	0	1
3	29	9	5	19	3	19	54	5

Aqueous phase, [metal nitrate] $= 1 \times 10^{-2}$ mol dm^{-3}; [picric acid] $= 2 \times 10^{-5}$ mol dm^{-3}; Organic phase, chloroform, [ligand] $= 1 \times 10^{-3}$ mol dm^{-3}; at 25°C for 24 h.

transition metals, have been reported [17]. This means the cyclic structure of **1** has a very important role in the formation of complexes with metal ions. The extractability of metal cations by **1** and **3** decreases in the sequence; $Hg^+ > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > Al^{3+} > Na^+ > K^+$ (**1**); $Hg^+ > Na^+ > Cu^{2+} \sim Cd^{2+} > K^+ > Ni^{2+}, Al^{3+}, Zn^{2+}$(**3**). It is very interesting to note that the order of selectivity of **1** and **3** for metal cations is quite different.

4. Conclusion

The title calixarene shows a strong ability for metal extraction from aqueous solution. The complexation pattern of **1** and copper ion in THF shows the complex to be of the 1:2 type. The high affinity of **1** for transition metals suggests that **1** could be a good support for attaching organometallic catalytic complexes as shown in the case of diphenylphosphino-polystyrene resins [18].

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