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The Transport Properties of Metal Picrates by Two New Calixarene Types

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ABSTRACT

The possibility of transporting several transition metal picrates (Cu^{2+}, Ni^{2+}, Co^{2+}, and Fe^{3+}) through an active transport membrane with a pH gradient was investigated. Two new macrocyclic ligands used as carriers, 5,11,17,23,29,35-hexa-*t*-butyl-37,38,39,40,41,42-hexakis-[*n*-(1-epoxyethyl)methoxy]calix[6]arene (I_6-EPO) and 5,11,17,23,29,35-hexa-*t*-butyl-37,38,39,40,41,42-hexakis-[*n*-(2-hydroxyaminoethyl)methoxy]calix[6]arene (I_6-HPA), were synthesized from *p-tert*-butylcalix[6]arene. It was found that the membrane system studied allows separation of some transition metal cations.

INTRODUCTION

Since Adams and Holmes discovered the ion-exchange properties of phenol-formaldehyde resins in 1935, much work has been directed toward the production of ion-exchange membranes (1). Various macrocyclic compounds have been used for transport. Calixarenes are a class of macrocyclic compounds prepared by the base-catalyzed condensation reactions of *p*-substituted phenols with formaldehyde (2). The oxygen functions of the latter offer many possibilities for manipulation of potential binding sites, and several groups have demonstrated how functional groups such as ester, ketone, ether, amide, thioamide, and carboxylic acid can be assembled as ligating side arms or podants for the reception of guest species, notably alkali, alkaline earth, and some transition metal cations (3–7). Shinkai and coworkers found that *p-tert*-butylcalix[6]arene can extract Cu^{2+} from an ammonia-alkaline solution to the organic solvent (8). Gutsche and Nam introduced dimethylamino groups onto the upper rim [this compound could bind Cu^{2+} and Ni^{2+} (9)]. In this paper the synthesizing, solvent extraction, and metal transport properties of *p-tert*-butylcalix[6]arene containing an epoxide and their amination compounds are studied.

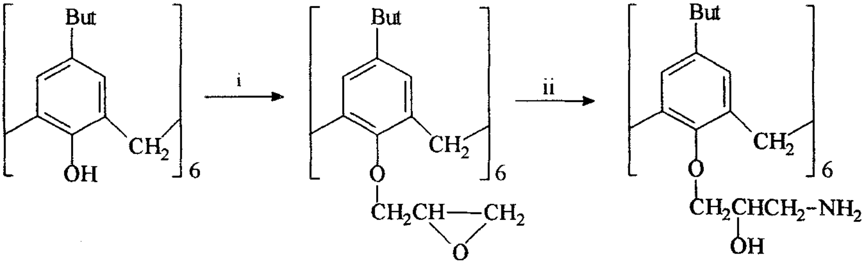
EXPERIMENTAL

Materials

The preparation of *p-tert*-butylcalix[6]arene (I_6) has been described previously (10). Metal nitrate solutions were prepared from the highest grade materials available using distilled, deionized water. Reagent spectrograde $CHCl_3$ was used as supplied. The IR spectra were measured using a Pye Unicam SP 1025 IR spectrometer in KBr pellets. The ^{1}H-NMR spectra were measured using a Varian T 100-A model spectrometer. The UV/VIS measurements were determined by using a Shimadzu 160 A model UV/VIS spectrophotometer with a 1-cm path-length.

Synthesis of I_6-EPO

One millimol *p-tert*-butylcalix[6]arene (I_6) was reacted with 10 mmol epichlorohydrine in acetone at room temperature for 36 hours in the presence of 1 mmol K_2CO_3 (Scheme 1). After the reaction time, the excess acetone was removed under low pressure, the product was washed two times with water, and then extracted with $CHCl_3$. $CHCl_3$ was removed, and a viscous product, 5,11,17,23,29,35-hexa-*t*-butyl-37,38,39,40,41,42-



I_6 I_6-EPO I_6-HPA

SCHEME 1 Reagents: i, epichlorohydrine; ii, ammonia.

hexakis-[*n*-(1-epoxyethyl)methoxy]calix[6]arene (I_6-EPO), orange-yellow in color, was obtained; mp > 300°C, yield 76%. IR (KBr): no ν_{OH}, $\nu_{epoxide}$ 1255–1260, 910 cm^{-1}; ^1H NMR ($CDCl_3$, 24°C) δ = 1.15 (t-Bu, s, 54H), 3.22 (epoxide, s, 6H), 3.96 ($ArCH_2$, s, 12H), 7.02 (ArH, s, 12H). Found: C, 77.08; H, 8.26%. Calculated for ($C_{84}H_{108}O_{12}$): C, 77.03; H, 8.31%.

Synthesis of I_6-HPA

One millimole I_6-EPO was reacted with an excess amount of ammonia for 18 hours at room temperature. The material obtained was dissolved in distilled water and filtered. Then the filtrate was concentrated to dryness. 5,11,17,23,29,35-Hexa-*t*-butyl-37,38,39,40,41,42-hexakis-[*n*-(2-hydroxy-aminoethyl)methoxy]calix[6]arene (I_6-HPA) was recrystallized from chloroform; mp > 300°C, yield 76%. IR (KBr): no ν_{OH} and $\nu_{epoxide}$. ^1H NMR ($CDCl_3$, 24°C) δ = 1.20 (t-Bu, s, 54H), 3.76 ($ArCH_2$, s, 12H), 5.46 (NH_2, br s, 12H), 7.21 (ArH, s, 12H). Found: C, 71.41; H, 8.92; N, 5.92%. Calculated for ($C_{84}H_{126}O_{12}N_6$): C, 71.46; H, 8.99; N, 5.95%.

Extraction Experiment

A chloroform solution (5 cm^3) containing calixarene and an aqueous solution (15 cm^3) containing metal picrate were placed in a flask. The aqueous solution was buffered to pH 2.0 with 10 $mmol{\cdot}dm^{-3}$ HCl-KCl (μ = 0.1 with KCl), pH 3.72 to 5.57 with 10 $mmol{\cdot}dm^{-3}$ acetate (μ = 0.1 with KCl). Extraction equilibrium was reached after 2 minutes of vigorous shaking by hand, followed by 60 minutes of magnetic stirring in the water bath at 24 ± 0.1°C. After the two phases were allowed to settle for 60 minutes, the absorbance of the aqueous phase was measured at 350 nm. A blank experiment without calixarene was run under the same conditions. The metal picrates were prepared by mixing metal nitrates and aqueous picric acid solution (5×10^{-7} $mol{\cdot}dm^{-3}$) until neutralization was reached as measured by potentiometry with a glass electrode (11). After precipitation, the picrates were filtered off and recrytallized from water.

Transport Experiment

Membrane transport experiments were conducted as reported earlier (12) by using a bulk liquid membrane apparatus (Fig. 1) based on the concept of the Schulman bridge (13). A chloroform solution (5 mL) containing carrier (7×10^{-5} M) was placed at the bottom of the apparatus. On the other phase was placed deionized water (10 mL), and at the top of the inside of the cylinder was carefully added 0.01 M metal picrate

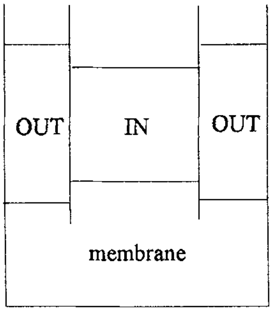


FIG. 1 Liquid-membrane system: IN and OUT phases are aqueous layers, membrane phase is the organic layer (in $CHCl_3$).

solution (10 mL). Thermolyne synchronous motors provided constant reproducible stirring at 100 rpm. The experimental units were maintained at 25°C. The appearance of the picrate anion in the outer phase was followed by a UV spectrophotometer ($\lambda_{max} = 350$ nm, $\epsilon = 1.5 \times 10^4$).

RESULTS AND DISCUSSION

Solvent Extraction and Stochiometry

In order to determine the extraction mechanism, plots of log D ($D = [\text{metal}]_{org}/[\text{metal}]_{aq}$, where aq and org denote the species in the aqueous and the organic phases, Eq. 2) versus pH were made, as shown in Fig. 2. For an extraction equilibrium:

$$M_{aq}^{n+} = [LH_m]_{org}[MLH_{m-n}]_{org} + nH_{aq}^{+} \tag{1}$$

$$D = \frac{[MLH_{m-n}]_{org}}{[M^{n+}]_{aq}} \tag{2}$$

The extraction equilibrium (K_{ex}) is given by Eq. (3). Equation (2) was reorganized as Eq. (4).

$$K_{ex} = \frac{[MLH_{m-n}]_{org}[H^+]_{aq}^{n}}{[M^{n+}]_{aq}[LH_m]_{org}} \tag{3}$$

$$\log D = n\,\text{pH} + \log K_{ex} + \log[LH_m]_{org} \tag{4}$$

Equation (4) indicates that the slope n for the log D versus pH plot corresponds to the number of protons released upon extraction. The plot for I_6-HPA results in a slope of 1.97. The results indicate that in solvent

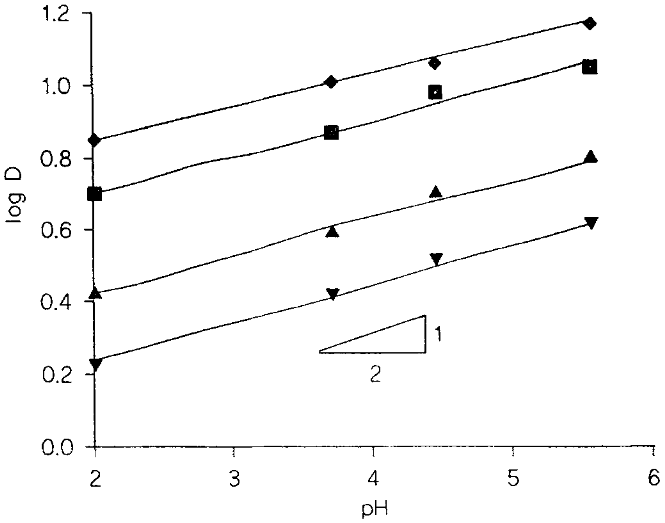


FIG. 2 Distribution coefficients of metal picrates as a function of pH. Aqueous phase: metal picrates of Ni^{2+} (■), Co^{2+} (▲), Cu^{2+} (▼), and Fe^{3+} (◆). Organic phase: I_6-HPA in chloroform.

extraction with I_6-HPA, the dissociation of two protons (i.e., an exchange between Ni^{2+} and $2H^+$) takes place at the water–chloroform interface.

In order to compare the complexation characteristics of I_6-EPO and I_6-HPA, the liquid–liquid extraction of several metal cations with the picrate ion into the solution of these compounds in chloroform was performed at 24 ± 0.1°C. The results obtained are summarized in Table 1. As can be seen from the table, the extraction efficiencies of the new calixarene vary considerably. Ex% values were calculated at each pH from Eq. (5).

$$\mathrm{Ex\%} = \frac{[\mathrm{M^+Pic^-}]_{\mathrm{org}} \times 100}{[\mathrm{M^+Pic^-}]_{\mathrm{aq}}} \qquad (5)$$

where $[M^+Pic^-]_{org}$ and $[M^+Pic^-]_{aq}$ are the metal picrate concentrations in the organic and water phases, respectively.

Metal Transport in a Liquid Membrane System

The transport rate in liquid membranes is dominated by diffusion within the unstirred layer near the phase boundary, and therefore the complexation process between the carrier (L) and cation (M) may be assumed to be at equilibrium. It is difficult to treat bulk liquid systems quantitatively

TABLE 1
Solvent Extraction of Metal Picrates from the Aqueous Phase to the Chloroform Phase (I_6-HPA) at 24 ± 0.1°C[a]

	log *D*	Extractability (%)	
Metal picrates	I_6-HPA	I_6-EPO	I_6-HPA
None	—	100	100
Cu^{2+}	0.754	20	85
Co^{2+}	0.667	38	82
Ni^{2+}	0.151	10	58
Fe^{3+}	0.030	3	11

[a] $[M^{2+}Pic^-] = 5 \times 10^{-7}$ mol·dm^{-3} in the aqueous phase (15 cm^3). pH 2.01 with 10 mmol·dm^{-3} acetate buffer. $[I_6\text{-HPA}] = 5 \times 10^{-4}$ mmol·dm^{-3} in chloroform (5 cm^3).

because of the dependence of the diffusion layer thickness upon cell geometry and stirring rate, but the main features of the results may be accounted for in terms of simple models, as in Fig. 3.

Here, the metal picrates transport ability of I_6-HPA in a liquid membrane system was tested. Metal picrates are extracted more efficiently at pH 5.57 than at pH 2.01. The pH of the IN aqueous phase was adjusted to pH 2.01–5.57. The OUT aqueous phase was kept acidic with 0.1 mol·dm^{-3} HCl to force decomplexation. In order to test if all metal picrate ions are carried from IN to OUT according to the active transport mechanism by the pH gradient, the quantity of I_6-HPA used was greater than that of the transported cations.

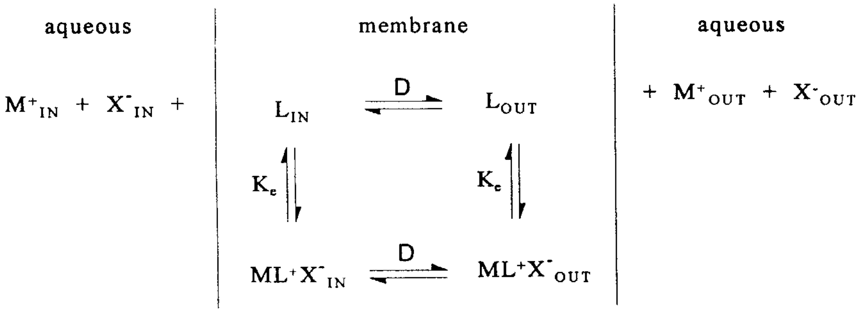


FIG. 3 Schematic representation of carrier (L) mediated transport of metal picrates in a liquid–membrane system.

In order to identify the rate-determining step, the rates of cation uptake and cation release were measured independently using the same transport apparatus. When cation uptake from the IN aqueous phase to the membrane phase was monitored, the OUT aqueous phase was replaced with air. After completion of the metal picrates extraction, the organic phase was separated and placed in a new membrane cell with the OUT aqueous phase. The rate of cation release was evaluated by following the metal picrates increase in the OUT aqueous phase. The result is illustrated in Fig. 4. Examination of Fig. 4 reveals that the rates determined independently for IN→membrane and membrane→OUT are in good agreement with those determined for the IN→membrane→OUT transport system. If the metal picrates extraction from the IN aqueous phase is the rate-determining step, the rate for membrane→OUT should be faster than that for the transport system. The good agreement between the independently determined rates and transport rates therefore supports the view that the rate-determining step in metal transport is the metal release to the OUT aqueous phase.

The transport rate of metal picrates by I_6-HPA is very fast. On the other hand, the transport rate by I_6-EPO is slower; after 60 minutes the mean

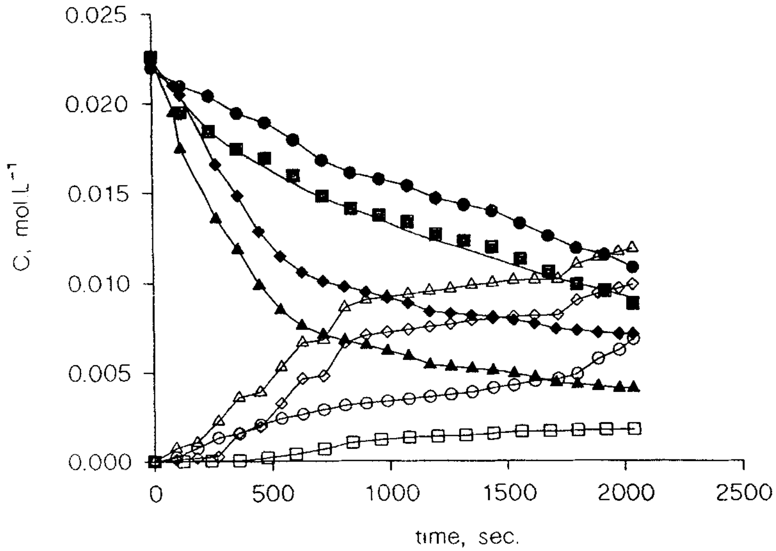


FIG. 4 The metal transport rate of I_6-HPA by the liquid–membrane system at pH 5.57: Ni^{2+} (■), Cu^{2+} (▲), Co^{2+} (◆), and Fe^{3+} (●).

rate of transport by carrier I_6-HPA is about 4 times faster than that by carrier I_6-EPO, as shown in Table 2. This difference in transport ability between carrier I_6-HPA and carrier I_6-EPO is remarkable. The complexation ability is higher than in I_6-EPO because I_6-HPA has amine groups that can be protonated. The transport rate of metal picrates by carrier I_6-HPA is constant after 60 minutes. Even when the concentration of metal picrates in the receiving phase is the same as that in the source phase after transport by carrier I_6-HPA, the transport rate of metal picrates by carrier I_6-HPA remains nearly constant.

For the purposes of the model, it is assumed that L and the complex ML are confined entirely within the membrane and the free salt is entirely within the aqueous phase. The diffusion reactions (assumed to proceed at equal rates for the ligand and complexed salt) include rapid transport by stirring between the diffusion layers at the IN and OUT faces. The equilibrium constant K_{ex} for complexation at the interface is defined by

$$K_{ex} = \frac{[\mathrm{ML}]_{\mathrm{IN}}}{[\mathrm{M}]_{\mathrm{IN}}[\mathrm{L}]_{\mathrm{IN}}} = \frac{[\mathrm{ML}]_{\mathrm{OUT}}}{[\mathrm{M}]_{\mathrm{OUT}}[\mathrm{L}]_{\mathrm{OUT}}} \tag{6}$$

The equilibrium assumption also provides a mass balance equation since the total concentration of carrier at every point must be equal (L_O). As a result, the concentration terms of Eq. (8) can be replaced by expressions involving K_{ex}, L_O, and the observable bulk concentrations M_{IN} and M_{OUT}. The final form of Eq. (7) is thus (14)

$$J_M = \frac{D}{2l} K_{ex} \frac{M_{IN} - M_{OUT}}{(1 + K_{ex}M_{IN})(1 + K_{ex}M_{OUT})} \tag{7}$$

Consideration of the limiting conditions for Eq. (7) is instructive. Assume that initially $M_{OUT} = 0$ and that throughout the experiment $M_{IN} \gg M_{OUT}$.

TABLE 2

Transport Rates and Extraction Equilibrium Constants of Metal Picrates by I_6-HPA and I_6-EPO in a Liquid Membrane System at 24 ± 0.1°C

	I_6-EPO		I_6-HPA	
Metal picrates	$J_{max} \times 10^{-4}$ mol·s^{-1}	$K_{ex} \times 10^3$ L·mol^{-1}	$J_{max} \times 10^{-2}$ mol·s^{-1}	$K_{ex} \times 10^3$ L·mol^{-1}
Cu^{2+}	4.20	3.79	2.11	195
Co^{2+}	3.87	3.70	1.95	186
Ni^{2+}	3.07	2.79	1.73	142
Fe^{3+}	2.80	2.71	1.41	137

When $K_{ex}M_{IN} \gg 1$, Eq. (7) becomes

$$J_M = \frac{D}{2l} K_{ex} \frac{M_{IN}}{(1 + K_{ex}M_{IN})} \tag{8}$$

Equation (8) is identical in form to the Michaelis–Menton equation derived for enzyme kinetics, and J_M behaves as a saturable process (15). As M_{IN} increases, J_M eventually achieves a maximum at

$$J_{max} = \frac{D}{l} \frac{[L]_0}{2} \tag{9}$$

In Eq. (9), l is the thickness of the diffusion layer and $[L]_0$ is the total concentration of carrier in the membrane. The transport kinetics are often treated in the same fashion as enzyme kinetics due to formal similarities between the two processes (15). As is clear from the above analyses, if $K_{ex} < K_{ex}(\max)$, the transport will behave as a saturable process. This is formally the same as a substrate and carrier forming a complex which, in a slow diffusional step, results in translocation. The rate can be related to the maximal rate through the Michaelis–Menton equations:

$$\frac{V}{V_{max}} = \frac{S}{K_m + S} \text{ (enzyme) } \frac{J}{J_{max}} = \frac{A}{K_m + A} \text{ (transport)} \tag{10}$$

where S and A are the substrate concentrations, V and J are the rates of the two processes, and K_m is the dissociation constant of the enzyme–substrate complex or the carrier–substrate complex. Thus, $K_m = 1/K_{ex}$ as defined above, since K_{ex} is effectively the association constant of the carrier–substrate complex. With this relationship, Eq. (10) is identical to Eq. (8) with the definition of J_{max} given in Eq. (9), and thus Eq. (10) will hold when the approximations leading to Eqs. (8) and (9) are valid, i.e., $A_{IN} \gg A_{OUT}$ and $K_{ex} < K_{ex}(\max)$. Having recognized the formal relationship, Eq. (10) can be exploited by using the methods of enzyme kinetics to yield the parameters of interest, J_{max} and $K_m = 1/K_{ex}$. Rearrangement of Eq. (10) gives the Lineweaver–Burke form (16):

$$\frac{1}{J} = \frac{K_m}{J_{max}A} + \frac{1}{J_{max}} \tag{11}$$

Experimental values of J at various concentrations of A can be treated by Eq. (11) to give K_m ($= 1/K_{ex}$) and J_{max} graphically (Fig. 5). In the double reciprocal form, $1/J_{max}$ appears as an intercept and K_m can be evaluated from the slope (K_m/J_{max}) or intercept at $1/J = 0$ ($-1/K_m$). The results obtained are summarized in Table 2.

These equations predict a simple proportionality of J_M to carrier concentration and, for a given concentration of ML, a transport efficiency

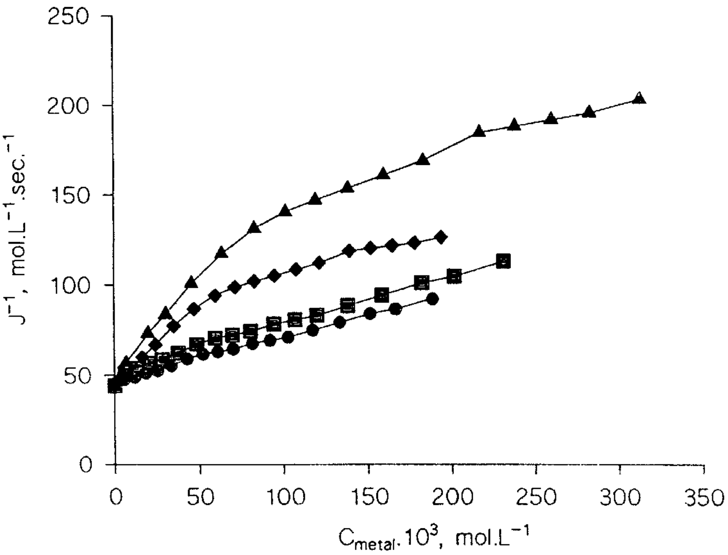


FIG. 5 The determination of J_{max} and K_{ex} graphically. Cu^{2+} (▲), Co^{2+} (◆), Ni^{2+} (■), and Fe^{3+} (●).

which increases with an increasing stability constant for complex formation between ligand and cation. They also illustrate, through K_{ex}, that the rate depends upon the nature of the accompanying cation. With increasing $[ML]_{IN}$, the rate increases to a maximum, J_{max}, when all of the carrier at the IN interface (and thus half of the total carrier) is complexed.

The metal picrate concentration in the receiving phase, which was monitored spectrophotometrically, increased linearly with time at a low transport fraction (initial rate conditions). The interfacial extraction constant was assumed to be linearly related to stability constants measure in chloroform. The results showed an excellent fit to Eq. (8), with a value of $l/D = 1.7 \times 10^{-3}$ s·cm^{-1}; this corresponds to a diffusion layer thickness of around 500 μm for diffusion coefficient $D \approx 10^{-4}$ cm^2·s^{-1}.

Table 2 lists the single-cation fluxes of Cu^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+} from the basic solution by the new calixarene types. The transport of Cu^{2+} was much greater than that of any of the other cations with the calixarene carriers. As with other ion-selective podants, the selectivities exhibited by the present calixarenes were strongly dependent on ionic size as indicated by the data in Table 2.

In order to understand more clearly the ion-binding properties of these new podants, we carried out transport rate determinations, and they were effectively governed by the metal ion size; this is consistent with the results of extraction experiments. A plot of moles of cation transported versus time was obtained for each system studied, and the rates of transport were estimated. Triplicate determinations were carried out for each cation–ligand pair, and in no case was transport of the cation across the chloroform membrane detected in the blank runs. The transport rates are collected in Table 2.

The results of transport experiments showed a similar trend to what was obtained in the extraction experiments, again confirming the unique participation of the amine and hydroxyl functions in the formation of complexes. However, an unexpected observation was that I_6-HPA did not exhibit efficient transport behavior, probably because it forms a tight complex with Cu^{2+}, thus becoming resistant to releasing the complexed cation into the other phase. The podant simply retains the cation in the chloroform layer.

In conclusion, the calixarenes show a strong ability for metal extraction from aqueous solution and active metal transport with a pH gradient in liquid membrane systems. The present study has demonstrated that transition metal picrates extraction and liquid membrane transport systems can be set up using calixarene-containing amine groups which exhibit remarkably high stability. The extraction and transport processes are related to pH values and metal ion size.

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