



the solvents were removed in vacuo. The  $^1\text{H}$  NMR spectrum of the white residue corresponding to the triacid chloride derivative was recorded to confirm its obtention; it was used without further purification for further synthesis. Trimethylsilyl chloride (5.50 mL, 43.33 mmol) was added dropwise to a solution of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (0.55 g, 7.92 mmol) in 25 mL pyridine at  $-10^\circ\text{C}$ . This mixture was stirred at this temperature for 30 min. Then, the triacid chloride calixarene derivative, dissolved in a minimum of  $\text{CH}_2\text{Cl}_2$ , was added dropwise. The reaction mixture was maintained at  $0^\circ\text{C}$  for 20 h, and evaporated in vacuo. The residue was treated with  $\text{CH}_2\text{Cl}_2$  and water and acidified with 1M HCl to pH 3. The separated organic layer was dried over  $\text{Na}_2\text{SO}_4$  and filtered. After evaporation of the solution to approximately half its volume, hexane was added to precipitate a yellowish solid which was chromatographed on a silica column with a 9:1 mixture of dichloromethane : methanol as an eluent.  $\text{L}^6\text{H}_3$  ( $R_f = 0.85$ ; same eluent as the column) was obtained as a white solid (m.p.:  $210\text{--}212^\circ\text{C}$ ) in 17% yield.

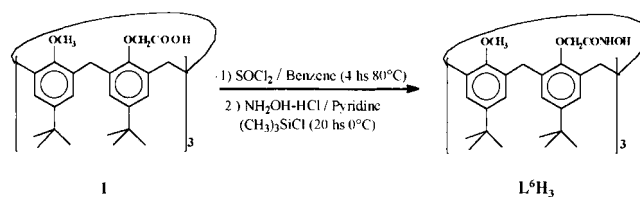
$^1\text{H}$ -NMR (9:1  $\text{CDCl}_3$ :  $\text{DMSO-}d_6$ )  $\delta$  8.69 (broad s, 3 H,  $-\text{NHOH}$ ), 7.99 (broad s, 3 H,  $-\text{NHOH}$ ), 7.32–6.41 (m, 12 H,  $\text{Ar}-\text{H}$ ), 5.15–4.21 (m, 18 H,  $\text{ArCH}_2\text{Ar}$  and  $\text{OCH}_2\text{CO}$ ), 2.50 (broad s, 9 H,  $-\text{OCH}_3$ ), 1.45–0.49 (m, 54 H,  $-\text{C}(\text{CH}_3)_3$ ). FAB MS  $m/z$  ( $\text{M}^+$ ) Calcd: 1234.62; found: 1234.1 (91%). Anal. Calcd for  $\text{C}_{75}\text{H}_{99}\text{N}_3\text{O}_{12}$ : C, 72.96; H, 8.08. Found C, 72.32; H, 8.09.

### Experimental

The extraction of transition metals:  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{4+}$ , and  $\text{Ag}^+$  by  $\text{L}^6\text{H}_3$  or LH was investigated using acetate and nitrate salts from Fluka (99%), Strem (99%) and Prolabo (99%). The organic solutions were made by dissolving a weighed amount of the ligand in the organic solvent: 1,2-dichloroethane from Fluka (99% purity) which was washed with distilled water before use (removal of the stabilizer). The aqueous solution was buffered to pH 5.3 with  $\text{CH}_3\text{COOH}$  (Prolabo 100%) ( $1.8 \times 10^{-3}$  M),  $\text{CH}_3\text{COONa}$  {Fluka (99%)} ( $8.2 \times 10^{-3}$  M); the ionic strength was maintained at  $\mu = 0.1$  with KCl (Carlo Erba 99.5%). Liquid-liquid extraction experiments were carried out in a flask by shaking (12 h;  $30^\circ\text{C}$ ) 25 mL of an aqueous phase containing metal salt ( $1.06 \times 10^{-4}$  M) and 5 mL of organic phase containing  $\text{L}^6\text{H}_3$  ( $5.3 \times 10^{-4}$  M) or LH ( $1.59 \times 10^{-3}$  M). The extraction was not affected by further shaking, indicating that the equilibrium had been attained. The aqueous phase was separated, centrifuged and subjected to analysis by atomic absorption spectrometry (Perkin Elmer 2380) with an air-acetylene flame or by ICP/AES (Varian-Liberty 220), the measurements being carried out using standard conditions for calibration. The extent of extraction (Ex %, Equation (1)) was determined from the uptake of metal concentration from the aqueous phase :

$$\text{Ex \%} = \left\{ \frac{([\text{Metal}]_{\text{blank}} - [\text{Metal}]_{\text{water}}) \times 100}{[\text{Metal}]_{\text{blank}}} \right\}, \quad (1)$$

where  $[\text{Metal}]_{\text{blank}}$  and  $[\text{Metal}]_{\text{water}}$  denote the metal concentration in the aqueous phase extracted with pure dichloro-



Scheme 1.

ethane and with the dichloroethane solutions containing extractants, respectively. The metal concentrations in the organic phase were determined by sampling the organic phase (2 mL) which was then stripped with 0.5 M of nitric acid (10 mL) (pH = 0.3) {Prolabo 68%}. Systematically, the mass balance was controlled, in order to check the validity of the measurements.

Membrane transport experiments were carried out in a U-shaped glass tube, section at the interface  $13.20\text{ cm}^2$ , immersed in a thermostated water bath at  $30^\circ\text{C}$  [24]. This cell was filled with 160 mL of  $5.3 \times 10^{-4}$  M solution of ligand in 1,2-dichloroethane interfaced to 80 mL of a  $1.06 \times 10^{-4}$  M solution of metal ions in one of the arms, and 80 mL of a 0.5 M solution of nitric acid in the another. A uniform mixer was inserted into each arm and two synchronous motors (Heidolph RZR 2000) provided a constant rotation (150 rpm), ensuring stirring of the phases. Transport across the organic phase was monitored by titration of metal ions in the source phase. At regular intervals, 2 mL of the source phase was sampled for spectrophotometric measurements. In order to maintain the position of the interfaces, 2 mL of the receiving phase were also removed. The variation of the volume of the phase was taken into account in the calculations.

### Results and discussion

The synthesis of ligand  $\text{L}^6\text{H}_3$  was conducted as shown in Scheme 1. 1,3,5-*O*-trimethyl-2,4,6-tris(-*O*-carboxymethyl)-*p*-*tert*-butyl calix[6]arene [22] **1** was treated with  $\text{SOCl}_2$  in benzene to afford the corresponding triacid chloride which was directly reacted with pertrimethylsilylated- $\text{NH}_2\text{OH}\cdot\text{HCl}$  in pyridine at  $0^\circ\text{C}$  for 20 h to afford the desired trihydroxamic acid  $\text{L}^6\text{H}_3$  in 17% yield. The structure of  $\text{L}^6\text{H}_3$  was deduced from the  $^1\text{H}$  NMR spectrum in 9:1  $\text{CDCl}_3$ : $\text{DMSO-}d_6$  which showed two broad singlets at 8.69 ppm ( $-\text{NH}$ ) and 7.99 ppm ( $-\text{OH}$ ) for the hydroxamic acid protons, the  $\text{FAB}^+$  MS with  $m/z = 1234.1$  at 91% and elemental analysis. A similar complexity of the  $^1\text{H}$  NMR spectrum has been reported for related  $\text{L}^6\text{H}_3$  showing very broad peaks [16].

In the individual extractions at pH 5.3,  $\text{L}^6\text{H}_3$  or LH extract more than 50% of  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pd}^{2+}$  (Figure 1). We observed that acetate, sodium and potassium ions, present in the aqueous solution, were not co-extracted. We concluded that these ions do not participate in the extraction process.

Apparently, no particular "calixarene effect" is observed in the extraction of  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pd}^{2+}$ . The enhancement

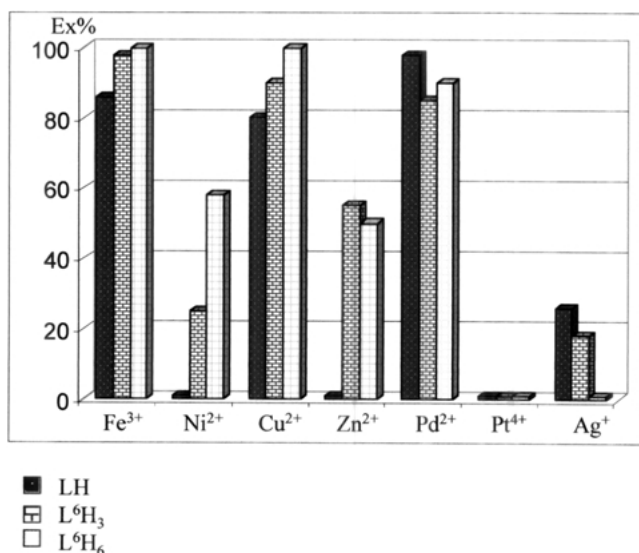
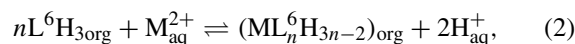


Figure 1. Extraction percentage of cations as a function of the nature of the ligands. Extraction from an aqueous solution of metal acetates (pH 5.3, [AcO<sup>-</sup>] = 0.01 M,  $\mu$  = 0.1, KCl, [M<sup>+</sup>] =  $1.06 \times 10^{-4}$  M) to organic solution at 30 °C ( $5.3 \times 10^{-4}$  M L<sup>6</sup>H<sub>3</sub> or L<sup>6</sup>H<sub>6</sub> or  $1.59 \times 10^{-3}$  M LH) in dichloroethane.

of zinc and nickel extraction passing from the monomer (LH) to a equivalent calixarene-hydroxamate concentration suggests a macrocyclic effect in these extractions.

Analysis of the extraction equilibria assumed the following general reaction for divalent cation:



with the corresponding constant:

$$K_{ex} = \frac{[ML_n^6H_{3n-2}]_{org} \times [H^+]_{aq}^2}{[M^{2+}]_{aq} \times [L^6H_3]_{org}^n}. \quad (3)$$

Introducing the distribution coefficient and taking the log form:

$$D_M = [ML_n^6H_{3n-2}]_{org}/[M^{2+}]_{aq} = M_{org}/M_{aq} \quad (4)$$

$$\log D_M = \log K_{ex} - n \log[L^6H_3] + 2 \text{pH}, \quad (5)$$

at constant pH,  $\log D_M = f(\log[L^6H_3])$  provides the stoichiometry of the extracted species

As shown in Figure 2 in the case of Zn<sup>2+</sup> the extraction analysis reveals the existence of a 1:1 complex. A similar analysis for Cu<sup>2+</sup> leads to the identification of a 1:2 M:L<sup>6</sup>H<sub>3</sub> complex, suggesting that no more than one chelate arm is bound in this case. This is in agreement with the fact that copper is extracted by monomer and by the calixarene hydroxamates at a similar level.

Molecular model examination of L<sup>6</sup>H<sub>3</sub> suggests that it is impossible to have square coordination (Cu<sup>2+</sup>) involving two arms of a common calixarene scaffold whereas trigonal-bipyramidal or tetrahedral geometry (Zn<sup>2+</sup>) is possible.

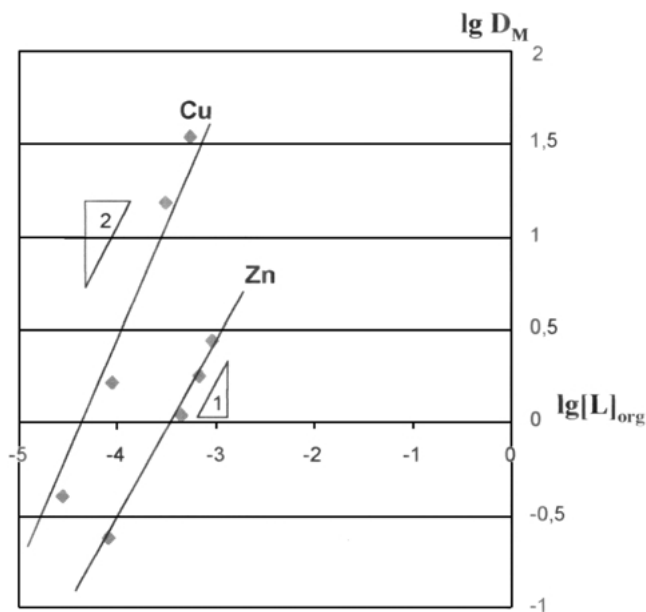


Figure 2. Standard  $\log D_M = f([L]_{org})$  plots with  $M = \text{Cu, Zn}$  and  $L = L^6H_3$ . Aqueous solution buffered to pH 5.3, [AcO<sup>-</sup>] = 0.01 M,  $\mu$  = 0.1, KCl, [M<sup>2+</sup>] =  $1.06 \times 10^{-4}$  M and organic solutions in dichloroethane. Temperature 30 °C.

A calixarene effect is also observed in the extraction of Pb<sup>2+</sup> by the monomer LH and L<sup>6</sup>H<sub>3</sub> whereas Cd<sup>2+</sup> is not extracted by hydroxamates.

Competitive extraction and transfer through a bulk liquid membrane were carried out for binary and ternary ion mixtures.

The results for the binary mixture Pb<sup>2+</sup>/Cd<sup>2+</sup> (Figure 3) showed that it is possible to separate Pb<sup>2+</sup> and Cd<sup>2+</sup> using L<sup>6</sup>H<sub>3</sub>. Pb<sup>2+</sup> is very flexible with regard to its coordination environment and the size of the cavity is better suited to Pb<sup>2+</sup> than to Cd<sup>2+</sup>.

This result is very important because the removal of lead, which is a toxic metal, can find numerous applications: in water quality assessment, wastewater treatment or fuel "depollution" [23].

The results for the ternary equimolar mixture of Fe<sup>3+</sup>: Cu<sup>2+</sup>: Cd<sup>2+</sup> (Figure 4) reveals the non-extraction of Cd<sup>2+</sup> and clearly shows the possibility to separate this cation from the two others within these particular pH conditions.

The competitive transport of the ternary equimolar mixture Cu<sup>2+</sup>: Ni<sup>2+</sup>: Zn<sup>2+</sup> shows that the transport rates follow the order of the individual extractions (Cu > Zn > Ni) (Figure 5).

## Conclusion

The present work has shown the influence of a macrocyclic effect in the extraction of zinc, lead and to a lesser extent nickel, by calixarene hydroxamates. The results might find practical applications in ion separations.

Further studies are in progress to obtain a more detailed understanding of the macrocyclic effect in the metal ions using calixarene hydroxamates. For this purpose we are

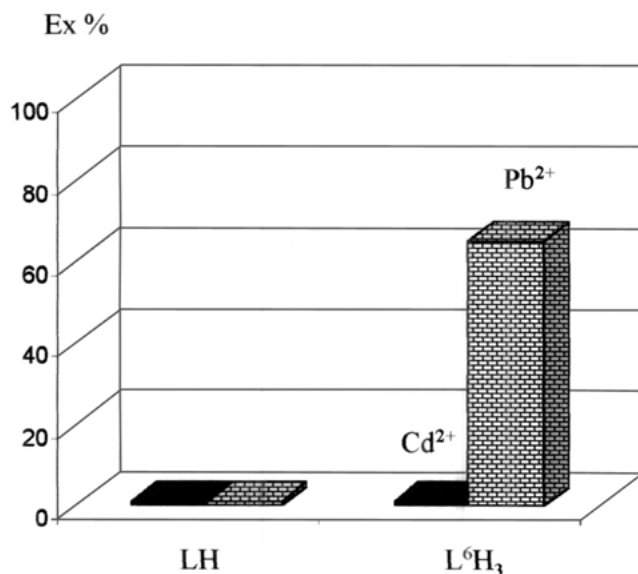


Figure 3. Competitive extraction of Cd<sup>2+</sup>/Pb<sup>2+</sup> by LH and L<sup>6</sup>H<sub>3</sub>. Aqueous solution (pH 5.3, [AcO<sup>-</sup>] = 0.01 M,  $\mu$  = 0.1, KCl, [M<sup>++</sup>] = 1.06 × 10<sup>-4</sup> M) to organic solution at 30 °C (1.59 × 10<sup>-3</sup> M LH or 5.3 × 10<sup>-4</sup> M L<sup>6</sup>H<sub>3</sub>) in dichloroethane.

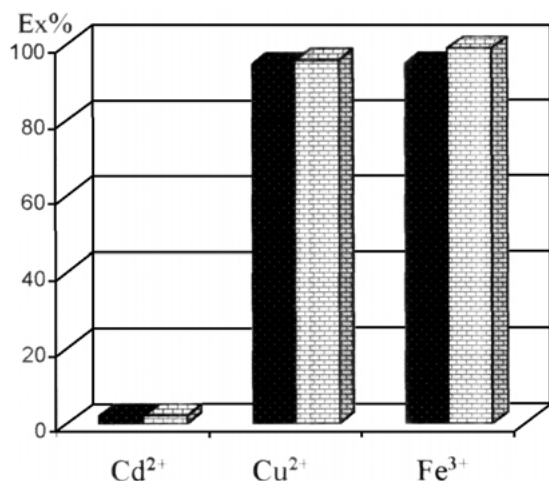


Figure 4. Competitive extraction of Cu<sup>2+</sup>, Cd<sup>2+</sup>, Fe<sup>3+</sup> by LH and L<sup>6</sup>H<sub>3</sub>. Extraction from an aqueous solution of metal acetates (pH 5.3, [AcO<sup>-</sup>] = 0.01 M,  $\mu$  = 0.1, KCl, [M<sup>2+</sup>] = 1.06 × 10<sup>-4</sup> M) to organic solution at 30 °C (1.59 × 10<sup>-3</sup> M LH or 5.3 × 10<sup>-4</sup> M L<sup>6</sup>H<sub>3</sub>) in dichloroethane.

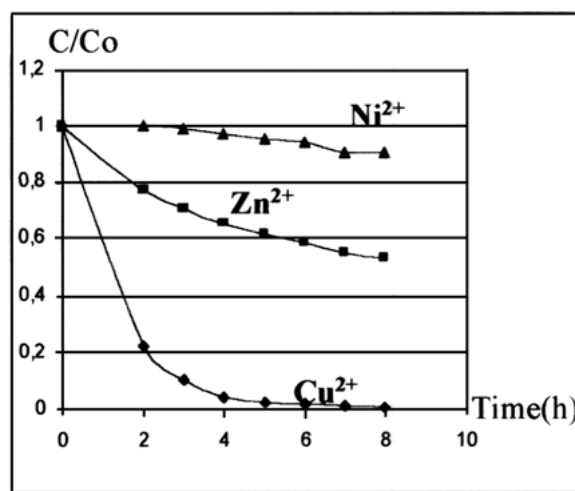
presently preparing linear oligomers of *p*-*tert*-butyl phenol units substituted with hydroxamic acid functions.

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C: [M<sup>++</sup>] in the source phase  
Co: [M<sup>++</sup>] at time 0

Figure 5. Time evolution of reduced concentration C/C<sub>0</sub> of Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> in the source phase in a competitive transport. Aqueous solution buffered to pH 5.3, [AcO<sup>-</sup>] = 0.01 M,  $\mu$  = 0.1, KCl, [M<sup>++</sup>] = 1.06 × 10<sup>-4</sup> M organic solution (5.3 × 10<sup>-4</sup> M L<sup>6</sup>H<sub>3</sub>) in dichloroethane. Temperature 30 °C.

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