p-tert-Butyldihomooxacalix[4]arene/*p-tert*-Butylcalix[4]arene: Transition and Heavy Metal Cation Extraction and Transport Studies by Ketone and Ester Derivatives

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Abstract

The binding properties of two phenylketones (**2a** and **3a**) and two ethylesters (**2b** and **3b**) derived from *p-tert*-butyldihomooxacalix[4]arene or from *p-tert*-butylcalix[4]arene, in the cone conformation, towards transition (Ag^+, Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Fe^{2+} and Mn^{2+}) and heavy (Cd^{2+}, Hg^{2+} and Pb^{2+}) metal cations have been determined by extraction studies with metal picrates and liquid membrane transport experiments with the same salts. The affinity of these ligands for Ag^+ has also been investigated by ^{1}H NMR spectroscopy. Both ketones are better extractants than the esters, and show a strong preference for Ag^+, while Cu^{2+} is the most extracted cation with the esters. ^{1}H NMR titrations with $AgSO_3CF_3$ indicate 1 : 1 complexes for all ligands, those with ketones are more stable, on the NMR time scale, than those with esters. Both esters are good carriers for Ag^+, and **2b** exhibits the highest transport rate (4.7 μmol h^{-1}) found until now with dihomooxacalix[4]arene derivatives.

Introduction

Over the last decade, calixarene applications [1–4] in the field of host-guest Chemistry have been the focus of intense research. Many of these studies deal with lower rim functionalized calixarenes and cationic guests, in particular alkali and alkaline earth metal cations. Transition and heavy metal cations have been less studied, although recently the study of their interactions with calixarenes has increased considerably [5, 6]. One of the reasons for this growth is certainly the harmful impact that some of these ions (like cadmium, mercury and lead), due to their toxicity, can provoke on environmental quality and consequently on human health, and the recognition that certain calixarene derivatives may be useful binders for these cations.

Despite the complexation of transition and heavy cations being favoured by the introduction of softer donor atoms such as nitrogen [7–13], sulphur [10, 14–18] or phosphorus [19], ligands with harder oxygen atoms can also bind these cations. These calixarenes bear phenoxy and carbonyl oxygens as the ligating sites, and include *N*-(X)sulfonylcarboxamides [20], hydroxamates [21, 22], amides [23–27], carboxylic acids [28–31], esters [23, 32, 33], and ketones [23, 33, 34]. Many of these studies have

been carried out on extraction/complexation of Ag^+, but data on other transition and heavy cations were also reported.

In the course of the studies of alkali and alkaline earth metal cation binding properties of dihomooxacalix[4]arene derivatives containing the carbonyl group at the lower rim [35, 36], we have extended our research into transition and heavy metals.

1   R = R₁ = H

2a   R = R₁ = CH₂COPh

2b   R = Me, R₁ = CH₂CO₂Et

3a   R = Ph

3b   R = OEt
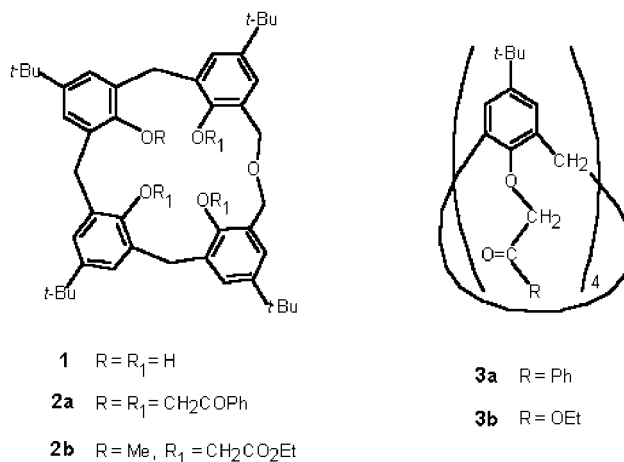
We report in this paper the binding properties of ligands **2a**, **2b**, **3a** and **3b** derived from

p-tert-butyldihomooxacalix[4]arene (**1**) or *p-tert*-butylcalix[4]arene, towards transition (Ag$^+$, Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Fe^{2+} and Mn^{2+}) and heavy (Cd^{2+}, Hg^{2+} and Pb^{2+}) metal cations. This has been assessed by extraction studies with metal picrates from aqueous solutions into dichloromethane and transport experiments with the same salts, through a dichloromethane membrane. The affinity of these ligands for Ag$^+$ cation has also been investigated by ^{1}H NMR spectroscopy.

Comparison is made between dihomooxacalix[4]arene derivatives and those of calix[4]arene in order to study the effects of their conformational flexibilities and the nature of the functional groups (ketone and ester) attached to the phenolic oxygens.

Experimental

Extraction studies

All four compounds used in extraction had already been prepared, and all possess the cone conformation in solution. **2a** and **2b** were synthesized in previous works [35], and **3a** and **3b** according to Arnaud-Neu *et al.* [37].

Equal volumes (5 mL) of aqueous solutions of metal picrates (2.5×10^{-4} M) and solutions of calixarenes (2.5×10^{-4} M) in CH$_2$Cl$_2$ were vigorously shaken for 2 min, and then thermostated in a water bath with mechanical stirring, at 25 °C overnight. After complete phase separation, the concentration of picrate ion in the aqueous phase was determined spectrophotometrically (λ_{max} = 354 nm). For each cation-calixarene system, the absorbance measurements were repeated four times. Blank experiments showed that no picrate extraction occurred in the absence of a calixarene.

Ni(II), Cu(II), Co(II), Zn(II), Mn(II), Cd(II) and Fe(II) picrates were obtained as described by Aggarwal *et al.* [38]. The first six picrates were prepared from the respective metal carbonate, and Fe(II) picrate was prepared by mixing together hot concentrated aqueous solutions of barium picrate and ferrous sulphate.

Due to the very low solubility of lead carbonate and lead hydroxide the reaction with picric acid was difficult, and the respective picrate was prepared from the acetate. An equivalent portion of that salt was added to a hot aqueous solution of picric acid. The stirred mixture was heated and concentrated to 25% of its volume. The remaining solution was removed by distillation in vacuum, leaving a solid residue which was dissolved in the minimum amount of hot water to give a mixture that was filtered. Recrystallization from water furnished lead picrate (PbPic$_2$·4H$_2$O) as yellow needles. The wet crystals were triturated and then washed with hot benzene and dried, to remove the unreacted picric acid.

Ag(I) and Hg(II) picrates were prepared *in situ* by dissolving freshly prepared metal oxide or hydroxide, respectively, in excess in a hot aqueous solution of picric acid. The mixture was stirred for 2–3 days and then filtered. After standing at room temperature for 24 h, the solution pH was measured, being in agreement with the theoretical value.
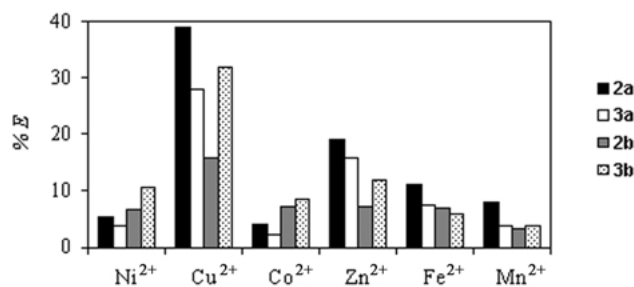

Figure 1. Percentage extraction (% *E*) of transition metal picrates into CH$_2$Cl$_2$ at 25 °C.

^{1}H NMR titration experiments

Several aliquots (up to 2–3 equiv) of a solution of AgSO$_3$CF$_3$ (1 M) in CD$_3$OD were added to CDCl$_3$ solutions (2×10^{-2} M) of the ligands directly in the NMR tube, with a 25 μl syringe. The spectra were recorded on a Varian Unity 300 spectrometer after each addition of the salt, and the temperature of the NMR probe kept constant at 22 °C.

Transport experiments

The ion transport across a liquid membrane was studied using an apparatus similar to that employed by Lamb *et al.* [39]. The membrane phase, 50 mL of CH$_2$Cl$_2$ containing the calixarene derivative (7×10^{-5} M), the receiving phase, 25 mL of doubly distilled and deionized water and the source phase, 7 mL of aqueous metal picrate solution (5×10^{-3} M), were placed in a thermostated vessel. The apparatus was maintained at 25 °C and the phases stirred at 150 rpm. The experiments were repeated, at least, three times. The appearance of the picrate ion in the receiving phase was followed by UV spectrophotometry at regular time intervals. The experimental procedure has already been described in detail elsewhere [35a].

In all cases, the plots of the number of moles transported to the receiving phase vs time, were linear, with correlation coefficients of at least 0.996. The slope of these straight lines represents the transport rate values. Experiments with no carrier present were performed, yielding a negligible transport rate, except in the cases of copper, lead and mercury, which was probably due to the formation of neutral complexes of these cations with picrate anion. These values were subtracted from those obtained with the calixarenes.

Results and discussion

Extraction studies

The ionophoric properties of compounds **2a**, **2b**, **3a** and **3b** towards transition and heavy metal cations were first investigated by the standard picrate extraction method [40]. The results, expressed as a percentage of cation extracted (% *E*) are collected in Table 1 and shown graphically in Figures 1 and 2.

These data reveal that the two ketones **2a** and **3a** have the same extraction profile, compound **2a** being a better phase

Table 1. Percentage extraction of transition and heavy metal picrates into CH_2Cl_2 at 25 °C[a]

	Ni^{2+}	Cu^{2+}	Co^{2+}	Zn^{2+}	Fe^{2+}	Mn^{2+}	Ag^+	Cd^{2+}	Hg^{2+}	Pb^{2+}
Ionic radius (Å)[b]	0.69	0.73	0.75	0.75	0.78	0.83	1.15	0.95	1.02	1.18
2a	5.5	39	4.0	19	11	8.0	74	13	10	9.1
3a	3.8	28	2.3	16	7.4	3.8	50	9.1	7.6	4.4
2b	6.8	16	7.1	7.1	6.9	3.4	15	4.1	5.7	8.8
3b	11	32	8.5	12	5.8	3.8	19	7.5	6.2	7.5

[a]Values with uncertainties less than 5%.
[b]R.D. Shannon and C.T. Prewitt; *Acta Crystallogr.* **B25**, 925 (1969); **B26**, 1046 (1970); data quoted in I. Marcus: *Ion Properties*, Marcel Dekker (ed.), New York (1997), pp 47–48.
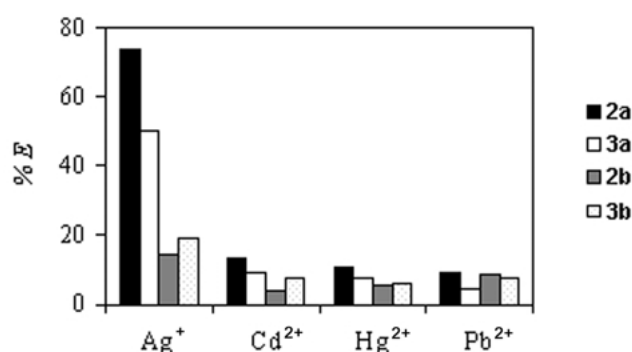

Figure 2. Percentage extraction (% *E*) of silver and heavy metal picrates into CH_2Cl_2 at 25 °C.

transfer agent than **3a**. Both ketones show a preference for Ag^+, Cu^{2+} and Zn^{2+}, and present little affinity for heavy cations (% *E* ranges from 9 to 13% for **2a** and from 4 to 9% for **3a**) and even less for the other transition cations (from 4 to 11% *E* for **2a** and from 2 to 7% *E* for **3a**).

The levels of extraction for Ag^+ are high with both ligands. In the case of **2a** (74%) this value is even higher than that obtained for K^+ (70%), while for **3a** (50%) it is only slightly lower than that of Na^+ (55%), the two most extracted cations within the alkali and alkaline earth series for these derivatives, respectively [35a]. The extraction level of Ag^+ exhibited by **2a** is comparable or even higher than those observed with some softer sulphur based ligands [17], and both **3a** and **2a** display strong Ag^+/Pb^{2+} selectivities: $S_{Ag^+/Pb^{2+}} = 11.4$ and 8.1, respectively.

Cu^{2+} and Zn^{2+} are also extracted by **2a** and **3a**, but Zn^{2+} only moderately (19 and 16%, respectively). For Cu^{2+} both ketones present values (39 and 28% for **2a** and **3a**, respectively) that are higher than those produced with Schiff base *p-tert*-butylcalix[4]arene derivatives bearing oxygen and nitrogen donor atoms [8], and also with some thioamides [16].

Ketone **2a** exhibits extraction percentages higher than those for ketone **3a** for all the cations studied. It seems that the dihomooxa derivative, with a larger cavity size, is a more flexible molecule and is therefore a better fit for all the cations.

Ester derivatives **2b** and **3b** are, in general, less efficient extractants than the ketones and among them **2b** is the most

inefficient. This derivative possesses only three ester groups with only six donating sites. Therefore, **2b** will surround the cations in a less efficient way. Moreover, it exists in a distorted cone conformation in solution, which may also contribute to its weak extracting ability [35b].

These ligands nearly show the same extraction profile being, however, the reverse of that shown by the ketones. Cu^{2+} is now the most extracted cation followed by Ag^+ and Zn^{2+} or Ag^+ and Pb^{2+} in the case of **3b** or **2b**, respectively. This selectivity pattern proceeds to Ni^{2+} and Co^{2+} (mainly for **3b**), whereas these cations are almost unextracted by the ketones, being the last ones in the extractability scale. Compound **3b** displays a good extracting power towards Cu^{2+}, superior to that exhibited by ketone **3a**.

The extraction of some of these cations (Ag^+, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Hg^{2+}) with ligand **3b** had already been reported [33], though under different experimental conditions. Although a comparison with our data is not valid, some remarks can be made. While the extraction levels for Ag^+ (68.5%) and Hg^{2+} (67.3%) are very superior to ours, it is nearly equal for Co^{2+} (9.4%) and are inferior for Cd^{2+} (1.2%), Ni^{2+} (3.7%) and for Cu^{2+} (6.0%).

Our results suggest that the match between the cation and the calixarene cavity dimensions is not an evident factor in selectivity. For example, Zn^{2+} and Co^{2+} have equal ionic radii and they are third and last, respectively, on the extractability scale, and also Ag^+ and Pb^{2+} having similar sizes are almost on the opposite ends of that scale, for both ketones. With ester ligand **3b** a similar situation is observed for Cu^{2+}, Zn^{2+} and Co^{2+}. Another important remark is that Cu^{2+} being one of the smallest divalent cations, is here the most extracted by ketone **2a**, which showed a strong selectivity for Ba^{2+} (57%) [35a], of nearly double the size.

On the other hand, the hard and soft acids and bases principle [41] does not seem to be an important factor in selectivity. Although our ligands contain hard oxygen donor atoms, they show a very clear preference for Ag^+, a soft Lewis acid, and Cu^{2+}, of intermediate nature. Moreover, the hard Lewis acid Mn^{2+} is one of the least extracted cations.

Therefore, no simple explanation for the observed selectivities is apparent from these results, and other factors involving the hosts and guests must be considered. For example, different conformational flexibilities of the calixarenes lead to different arrangements of the donor atoms in
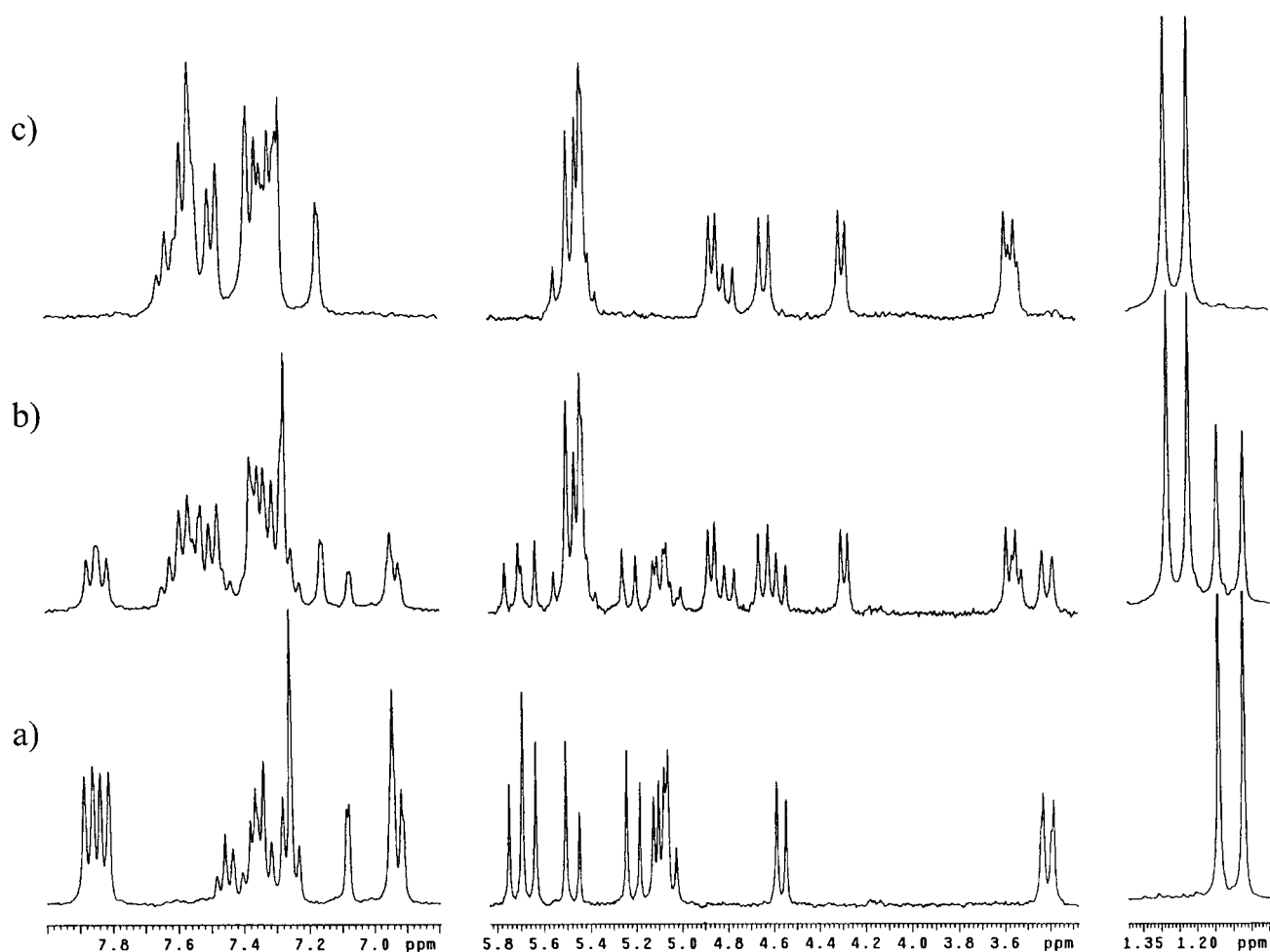
Figure 3. 300 MHz ^{1}H NMR spectra of ketone **2a** in CDCl$_3$ at 22 °C. (a) free ligand, (b) upon addition of 0.5 and (c) 1 equiv of AgSO$_3$CF$_3$.

^{1}H NMR studies

Further information on the cation binding behaviour of the dihomooxacalix[4]arene and calix[4]arene derivatives was obtained by ^{1}H NMR titration experiments. Variable amounts of silver triflate were added to derivatives **2a**, **2b**, **3a** and **3b**, and the proton spectra were recorded after each addition.

Two different situations were found after the addition of the salt to the compounds. Titration of both ketones (**2a** and **3a**) with AgSO$_3$CF$_3$ shows that, with a [salt]/[ligand] ratio lower than 1, both signals of the complexed and uncomplexed ligands are present in the spectrum (Figure 3), indicating that on the NMR time scale the exchange rate between the two species is slow, at room temperature. With a 1 : 1 ratio, all the signals for the free ligand disappeared and those of the complexed ligand remain unchanged after subsequent additions of the salt, indicating a 1 : 1 metal-ligand stoichiometry. In contrast, titration of esters **2b** and **3b** with AgSO$_3$CF$_3$ induces broadening of the signals until the [salt]/[ligand] ratio reaches the unity value, when the signals become sharp (Figure 4). This indicates exchange

rates comparable with the NMR time scale, at room temperature. Again, ^{1}H NMR titration experiments suggest a 1 : 1 stoichiometry for the AgSO$_3$CF$_3$ complexes with ester ligands, since no further spectral changes are observed after subsequent additions of the salt.

These data show that the exchange rates for Ag$^+$ with esters **2b** and **3b** are faster than those with the ketones, and consequently that Ag$^+$ cation must be more tightly encapsulated inside the ketone ionophoric cavities than in those of the esters. These observations agree with the extraction results, which have shown a much lower affinity of ester ligands for Ag$^+$ than the ketones.

^{1}H NMR data of the free and complexed ligands **2a**, **3a** and **3b** with silver triflate are collected in Table 2.

Upon complexation all proton chemical shifts in the ligands change. The largest variation is recorded for the bridging axial methylene protons and by the methylene protons of the OCH$_2$CO groups, which move upfield, and by the aromatic protons of the calixarene skeleton, which move downfield. The smallest variation is observed for the protons of the *tert*-butyl groups. Similar situations have been found for closely related calix[4]arene derivatives with Na$^+$ [26, 42] and Ag$^+$ cations [34].

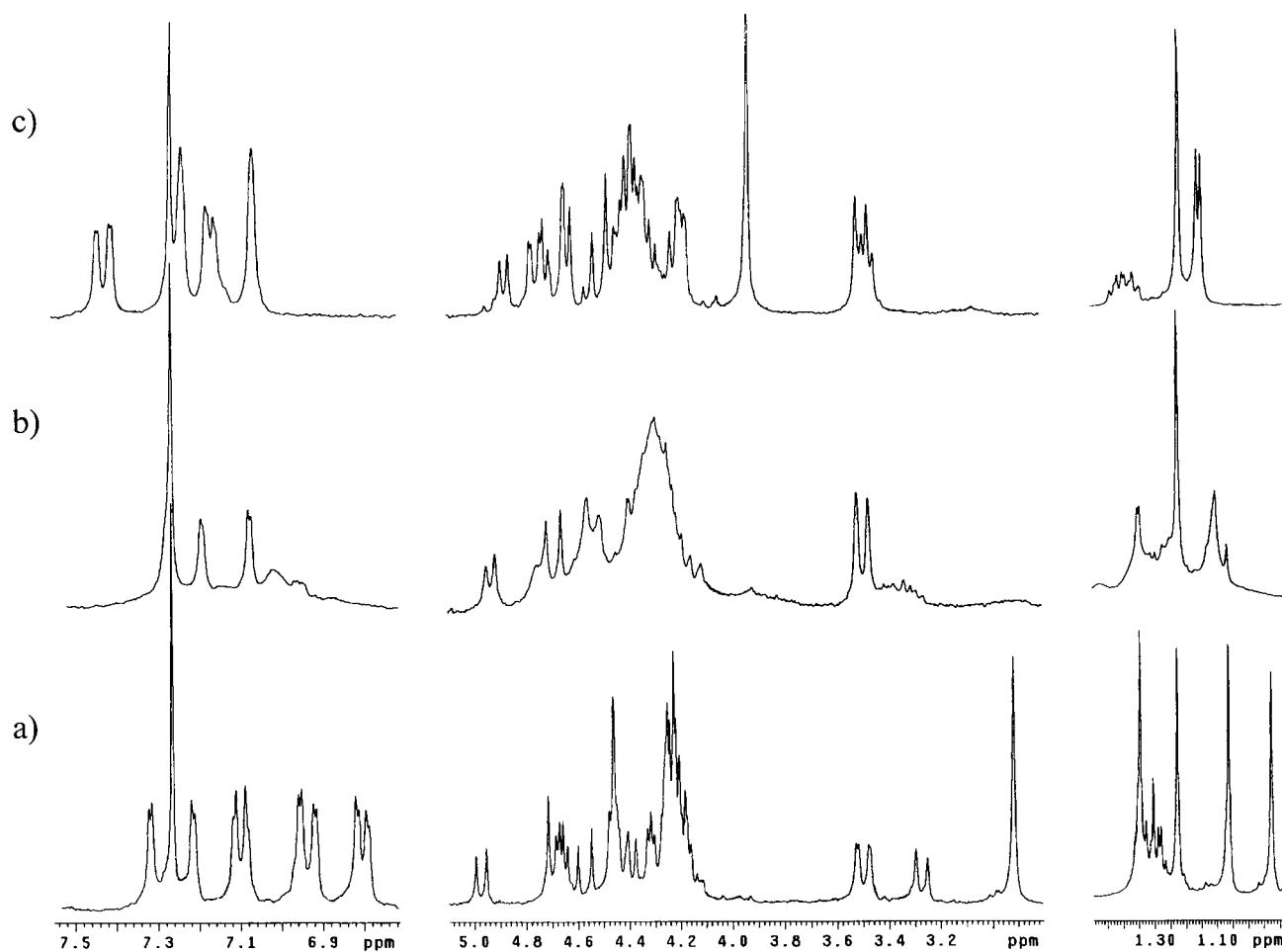The largest upfield shifts undergone by the complexed ligands on protons adjacent to the oxygen donor atoms,

Figure 4a. 300 MHz ^{1}H NMR spectra of ester **2b** in CDCl$_3$ at 22 °C. (a) free ligand, (b) upon addition of 0.5 and (c) 1 equiv of AgSO$_3$CF$_3$.

Table 2. Relevant proton chemical shifts (δ, ppm) of ligands **2a**, **3a**, and **3b** and their complexes with AgSO$_3$CF$_3$

	t-Bu	ArCH$_2$Ar		CH$_2$OCH$_2$		OCH$_2$CO	ArH
		eq	ax	eq	ax		
2a	1.07, 1.14	3.41, 3.42	5.10, 5.05	4.57	5.08	5.21, 5.48, 5.67, 5.72	6.91, 6.94, 6.95, 7.08
2a + Ag$^+$	1.22, 1.28	3.57, 3.55	4.63, 4.75	4.29	4.86	5.37–5.55	7.17–7.36
3a	1.11	3.27	5.12			5.70	6.84
3a + Ag$^+$	1.21	3.50	4.47			5.33	7.24
3b	1.07	3.19	4.85			4.81	6.78
3b + Ag$^+$	1.17	3.44	4.32			4.45	7.17

can be explained in terms of cation binding to those donor atoms, causing marked conformational changes. Therefore, this suggests that the cation must be inside the cavity defined by the phenoxy and carbonyl oxygen atoms. The downfield shift for the aromatic protons indicates the involvement of the phenolic oxygens in complexation, as reported by Ungaro *et al.* [42].

The variation in chemical shift experienced by the equatorial methylene protons is downfield and much smaller than that of the axial protons for the three compounds, but for dihomooxaketone **2a** the CH$_2$OCH$_2$ resonances behave differently. Here, both axial and equatorial methylene protons move upfield and with approximately the same value ($\Delta\delta$ =

0.22 and 0.28 ppm, respectively). This result suggests that the oxygen bridge conformation changes upon complexation, with both CH$_2$ protons undergoing a similar shielding effect.

Relative to **2b**, being an entirely asymmetrical molecule, it is difficult to make a complete assignment for the complexed ligand only from the proton spectrum. However, this derivative seems to show variations in the same directions as the others, and mainly exhibits a high downfield shift ($\Delta\delta$ = 1.02 ppm) for the methyl protons of the OCH$_3$ group, due to the interaction of the oxygen atom with Ag$^+$ cation.
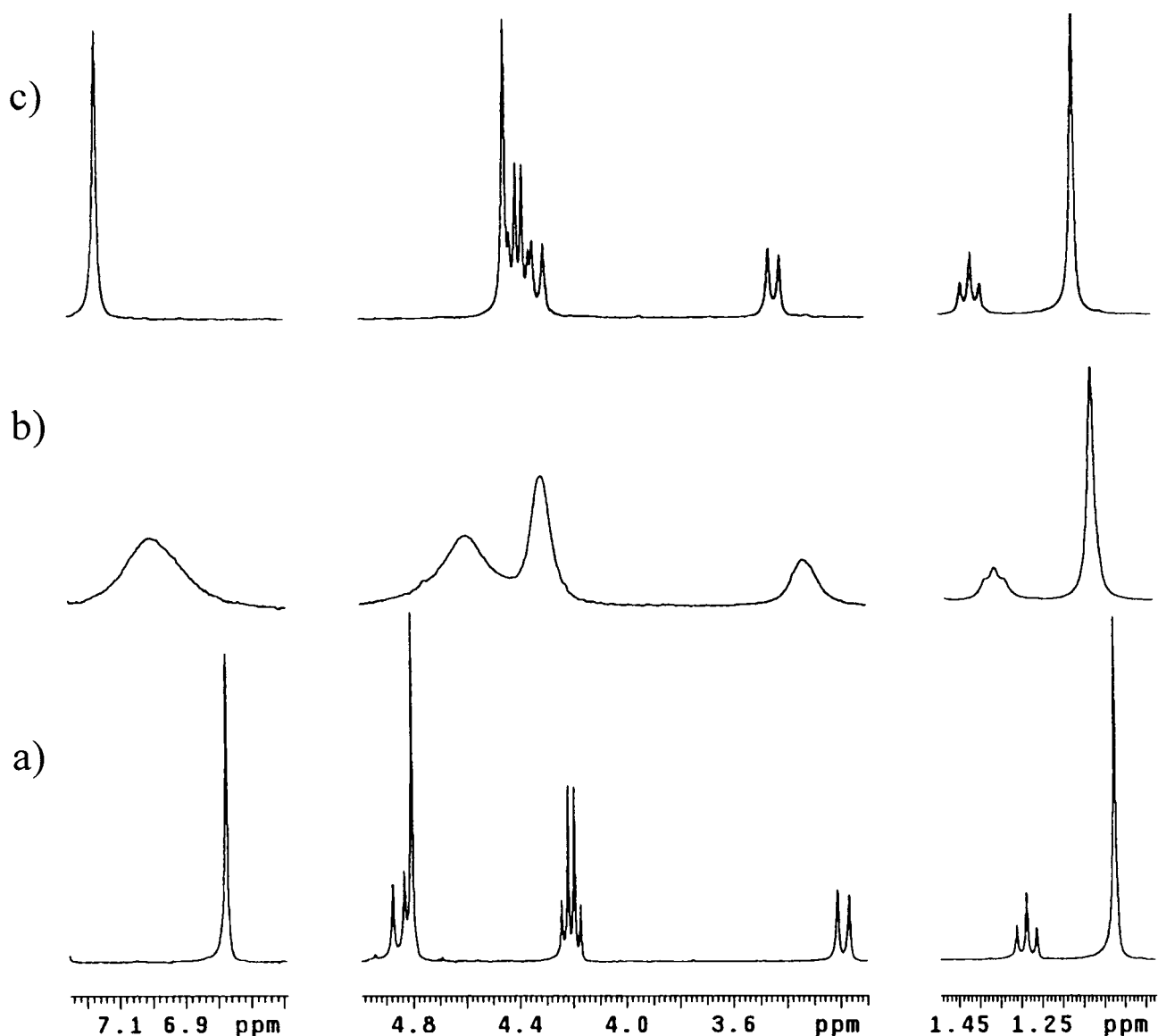
Figure 4b. 300 MHz ^{1}H NMR spectra of ester **3b** in CDCl$_3$ at 22 °C. (a) free ligand, (b) upon addition of 0.5 and (c) 1 equiv of AgSO$_3$CF$_3$.

Ion transport across a liquid membrane

Transport experiments were carried out in a CH$_2$Cl$_2$ liquid membrane system, similar to that employed by Lamb *et al.* [40]. Table 3 and Figures 5 and 6 present the transport rates V, in μmol h^{-1}, for compounds **2a**, **2b**, **3a** and **3b**.

Table 3 shows that the four ligands are inefficient neutral carriers for all divalent transition cations (V ranging from 0.01 up to 0.09 μmol h^{-1}), with the exception of the systems **2b**-Cu^{2+} and, to a smaller extent, **2b**-Zn^{2+} and **2a**-Cu^{2+} (0.9, 0.38 and 0.21 μmol h^{-1}, respectively).

Relative to heavy metal cations, both ketones and ester **3b** display reasonable transport rates, except for Cd^{2+}. **2b** is a more efficient carrier that the other ligands, and shows a high transport rate for Pb^{2+} (2.3 μmol h^{-1}). Ester **3b** and ketone **3a** show a preference for Hg^{2+}, and ketone **2a** exhibits a weak discrimination between Pb^{2+} and Hg^{2+} cations.

Ag$^+$ is moderately carried by the ketones, while the ester ligands show a much higher transport rate for this cation. Among the esters, **2b** is the most efficient with a transport rate of 4.7 μmol h^{-1}. Until now, this is the highest value found with our dihomooxacalix[4]arene derivatives for all the cations studied. However, ester **3b** shows the biggest Ag$^+$/Pb^{2+} selectivity ($S_{Ag^+/Pb^{2+}}$ = 15.3).

Interestingly, derivative **2b** is now the best carrier in contrast to the extraction process, where it was the worst extractant. Ligands **2a**, **3a** and **3b** have almost equal efficiencies, but clearly inferior to that of **2b**. As discussed above, **2b** is the most flexible ligand and the poorest phase transfer agent, showing a weak affinity for the cations. Hence, it is expected that it rapidly releases the cations at the interface with the receiving phase, being a better carrier than receptor. A similar situation was already found with alkali and alkaline earth metal cations [35b].

The trend found in transport for compound **2b** seems, to some extent, to follow that of extraction. With some ex-

Table 3. Transport rate (V/μmol h^{-1}) of transition and heavy metal picrates through a CH$_2$Cl$_2$ liquid membrane at 25 °C[a]

	Ni^{2+}	Cu^{2+}	Co^{2+}	Zn^{2+}	Mn^{2+}	Ag$^+$	Cd^{2+}	Hg^{2+}	Pb^{2+}
2a	0.032	0.21	0.023	0.049	0.046	0.8	0.08	0.8	1.0
3a	0.029	0.09	0.016	0.033	0.032	0.48	0.035	1.7	1.0
2b	0.09	0.9	0.09	0.38	0.05	4.7	0.49	0.8	2.3
3b	0.012	0.06	0.009	0.032	0.021	2.3	0.036	0.9	0.15

[a]Reproducibility of ±10%.

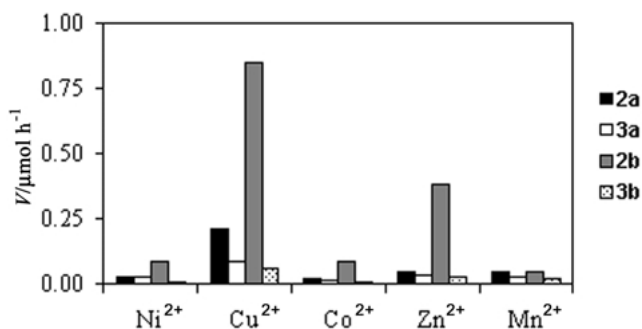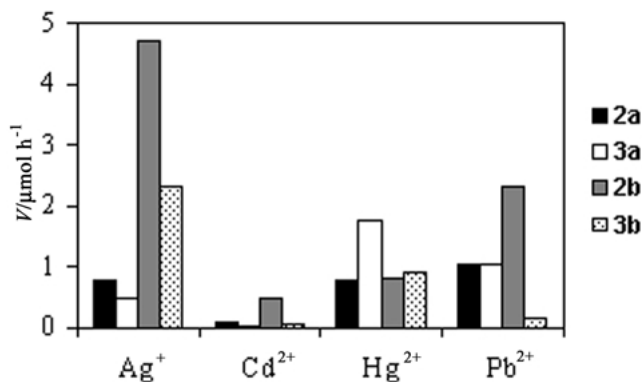*Figure 5.* Transport rate ($V/(\mu$mol h^{-1})) of transition metal picrates through a CH$_2$Cl$_2$ liquid membrane at 25 °C.

Figure 6. Transport rate ($V/(\mu$mol h^{-1})) of silver and heavy metal picrates through a CH$_2$Cl$_2$ liquid membrane at 25 °C.

ceptions, the other compounds (**2a**, **3a** and **3b**) exhibit a trend in extraction that seems the reverse of that observed in transport. For example, while Pb^{2+} and Hg^{2+} are the most carried cations with **2a**, they are only modestly extracted by this ligand.

Conclusions

Extraction studies with transition and heavy metal picrates from an aqueous solution into CH$_2$Cl$_2$ have shown that both ketones are better phase transfer agents and also more selective than the esters. This indicates a higher affinity of the cations for the functional ketonic group due to the higher basicity of the carbonyl group, than to the functional ester group. Ag$^+$ and Cu^{2+} are the most extracted cations by the ketones, while esters show the reverse preference (Cu^{2+} and Ag$^+$). The best extractant is dihomooxaketone **2a**, whereas the more rigid ketone **3a** is the most selective. Dihomoox-

aester **2b** is the most flexible ligand and displays a plateau selectivity with little discrimination between the cations. Nevertheless, this derivative is the best carrier, showing the highest transport rate for Ag$^+$ (4.7 μmol h^{-1}). This value is even the highest found until now with our dihomooxa compounds.

All compounds form 1 : 1 complexes with Ag$^+$, and the cation is believed to be encapsulated into the cavity defined by the phenoxy and carbonyl oxygen atoms. The results have shown that, although these ligands bear hard oxygen donor atoms, they display a strong affinity towards soft metal cations, like Ag$^+$ and Cu^{2+}.

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