

Calix[4]arenes with Pendant Amide and Phosphine Oxide Functionalities: Use as Extractive Agents and Carriers for Silver (I) Ions

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(Received: 17 October 1996; in final form: 16 January 1997)

Abstract. The solvent extraction properties towards Ag^+ of 5,11,17,23-tetra-*tert*-butyl-25,27-diX-26,28-bis(diphenylphosphinoylmethoxy)calix[4]arenes (X = $\text{CH}_2\text{C}(\text{O})\text{NEt}_2$ (**1**), $\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ (**2**), CH_3 (**3**), $\text{CH}_2\text{C}(\text{O})\text{Et}$ (**4**)) have been studied. Each ligand forms a 1 : 1 complex with silver(I). Ligand **1**, which bears two amide functionalities, is the most efficacious, emphasizing the crucial role played by the polar amide groups. The rate of transport of AgNO_3 through a bulk liquid membrane with this ligand as carrier was shown to be superior to that of DC18C6, a structurally-related multi-oxygen donor carrier. NMR and IR data suggest that Ag^+ is coordinated to each of the oxygen atoms in the ligand leading to an encapsulated structure $[\text{Ag} \subset \mathbf{1}]^+$.

Key words: Calixarene, amide, phosphine oxide, silver, extraction, transport.

1. Introduction

Among synthetic macrocyclic compounds, calixarenes [1] are of particular interest as metal ion receptors. Calix[4]arenes bearing neutral substituents attached to the phenolic oxygen atoms (i.e. functionalized at the lower rim) have been shown to exhibit interesting complexation, extraction and transport properties with respect to alkali and alkaline earth cations [2].

Despite the increasing use of calixarenes as ligands for transition metals [3], few investigations have been concerned with the selective complexation of silver(I) by calix[4]arenes. Recent studies by Ikeda *et al.* [4] and by Xu *et al.* [5] have shown that tetra O-alkylated calix[4]arenes, in various conformations, are able to bind a silver ion inside the cavity defined by the four aryl rings via $\text{Ag}-\text{C}$ π -bonding. In these structures, the metal ion is located between two *p*-carbon atoms

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of distal aryl rings. This situation contrasts with the complexation of silver ions by the calixspherands recently reported by Reinhoudt *et al.*, where bonding primarily involves the methoxy oxygen atoms of the lower rim [6]. It should be emphasized that in all these systems complexation of silver is weak, so that such ligands do not appear to be well suited for use in extractive procedures. However, another approach to this goal has been reported very recently by Ohto *et al.* who described the extraction of silver in the presence of palladium(II) by a calix[4]arene-derived tetraketone [7].

In previous work we have described the selective binding and transport properties of two new calix[4]arenes; namely, the mixed diamide–diphosphine oxide **1** and the tetraphosphine oxide **2** (Figure 1) as extractive agents and carriers for alkali cations [8]. This study described the ability of these ligands to encapsulate sodium and potassium inside the ionophoric cavity of the tetrapodes. Calixarene **1** exhibited better extraction and transport properties of alkali cations than **2**.

In the present paper we describe the extractive properties of **1** and **2**, together with those of the corresponding dimethoxy-di(phosphine oxide) **3** and the diester-di(phosphine oxide) **4** towards silver nitrate. The results are compared with those of a conventional multi-oxygen donor, DC18C6. We consider the transport of silver nitrate by **1** through a bulk liquid membrane in terms of a mathematical model proposed earlier [9]. The coordination geometry about the $[\text{Ag} \subset \mathbf{1}]^+$ complex is also discussed.

2. Experimental

2.1. MATERIALS AND INSTRUMENTATION

Ligands **1**, **2** and **4** were synthesized according to the procedure described previously [10–12]. Dicyclohexano-18-crown-6 (DC18C6) was used as received (Fluka). Dichloromethane, used for extraction and transport experiments, was washed several times with distilled water. Silver nitrate (Aldrich), copper nitrate (Janssen Chimica) and all other reagents were analytical grade. Solvents used for synthesis were dried by conventional methods and distilled immediately prior to use. For ^1H -NMR experiments CDCl_3 was passed through a 5 cm thick alumina column and stored under argon over molecular sieves (0.4 nm). IR spectra were recorded on a Perkin Elmer 1600 spectrometer ($4000\text{--}400\text{ cm}^{-1}$). ^1H -, $^{31}\text{P}\{^1\text{H}\}$ -, and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded on a FT Bruker WP-200 SY instrument. The ^1H -NMR data were referenced to residual protiated solvents (7.27 ppm for CDCl_3), ^{13}C chemical shifts are reported relative to deuterated solvents (77.0 ppm for CDCl_3) and ^{31}P -NMR data are given relative to external H_3PO_4 . Mass spectra were recorded on a ZAB HF VG Analytical instrument using *m*-nitrobenzyl alcohol or tetraglyme as matrix.

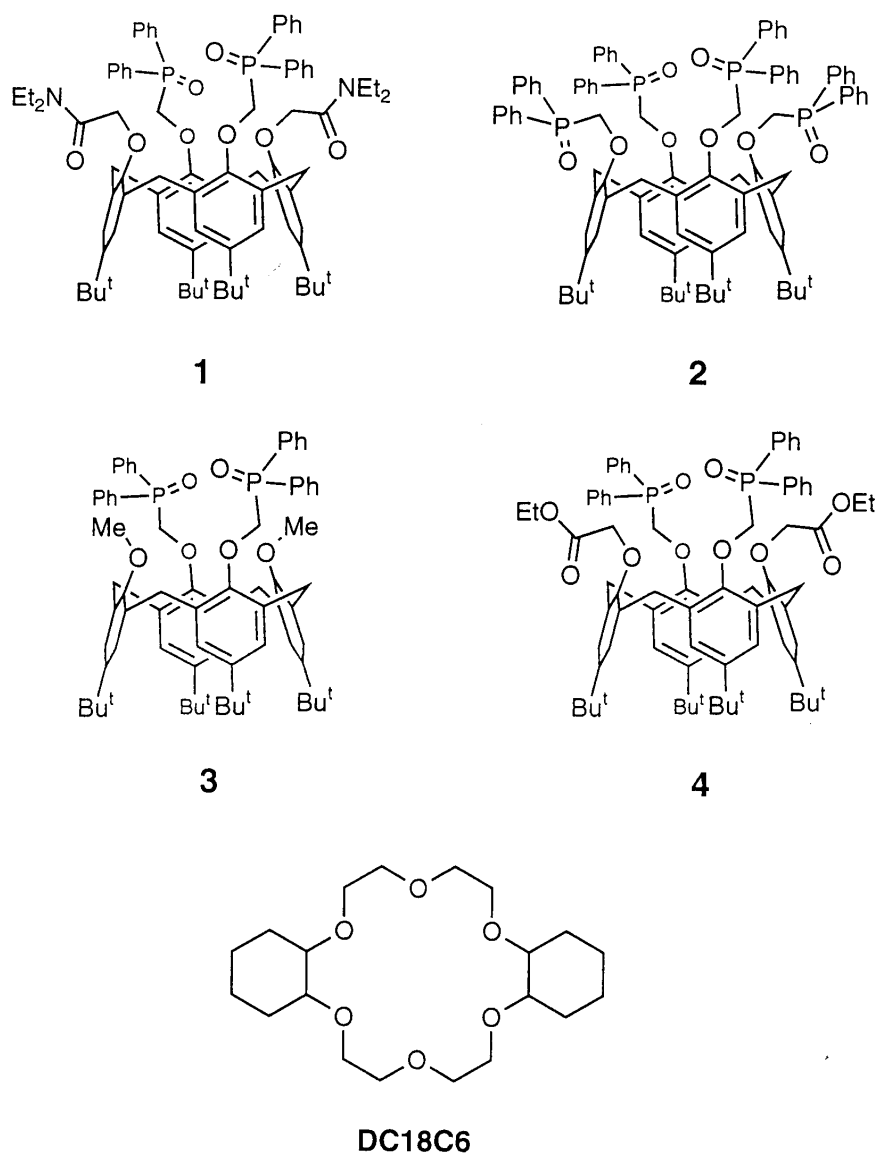


Figure 1. Ligands used in this work.

2.2. SYNTHESSES

2.2.1. 5,11,17,23-Tetra-tert-butyl-25,27-dimethoxy-26,28-dihydroxycalix[4]arene, precursor for **3**

A suspension of *p*-tert-butylcalix[4]arene (5.000 g, 7.70 mmol), K₂CO₃ (1.170 g, 8.47 mmol) and MeC₆H₄-*p*-SO₃Me (2.868 g, 15.40 mmol) in CH₃CN (200

mL) was refluxed for 30 h. The solution was filtered and the solvent was removed *in vacuo*. The residue was then dissolved in CH₂Cl₂ (300 mL) and the solution was washed three times with water (100 mL). The aqueous phase was neutralized with 1 M HCl. The organic phase was dried over MgSO₄. After filtration and concentration, the product was precipitated with hexane and recrystallized from CH₂Cl₂/hexane yield 4.950 g, 95%, m.p. 248–250 °C. IR (KBr) : ν_{OH} 3445 br cm^{-1} . ¹H-NMR (CDCl₃, 25 °C): δ 7.26 (s, 2H, OH), 7.07 (s, 4H, *m*-ArH), 6.78 (s, 4H, *m*-ArH), 4.29 and 3.33 (AB spin system, 8 H, ArCH₂Ar, ²*J* = 13.1 Hz), 3.95 (s, 6H, OMe), 1.30 (s, 18H, Bu^t), 0.95 (s, 18H, Bu^t). ¹³C{¹H}-NMR (CDCl₃): δ 151.18, 150.52, 146.80, 141.46, 132.27 and 127.89 (6s, aromatic C_{quat}), 125.54 and 125.06 (2s, aromatic CH), 63.50 (s, OCH₃), 33.86 and 33.87 (2s, C(CH₃)₃), 31.76 and 31.03 (2s, C(CH₃)₃), 31.40 (s, ArCH₂Ar). *Anal. Calcd.* for C₄₆H₆₀O₄ (*M_r* = 676.99): C, 81.61; H, 8.93. *Found:* C, 81.70; H, 8.90.

2.2.2. 5,11,17,23-Tetra-*tert*-butyl-25,27-dimethoxy-26,28-bis(diphenylphosphino)methoxycalix[4]arene **3**

5,11,17,23-Tetra-*tert*-butyl-25,27-dimethoxy-26,28-dihydroxycalix[4]arene (2.031 g, 3.00 mmol) was treated with NaH (0.194 g, 8.08 mmol) in 150 mL of a THF–DMF mixture (9 : 1, v/v). The solution was stirred at reflux temperature for 1 h. After addition of Ph₂P(O)CH₂OTs [13] (2.900 g, 7.50 mmol), the solution was refluxed for a further 48 h. The mixture was then evaporated to dryness. The residue was recrystallized from ethanol/water: yield 3.02 g, 91%, m.p. 236–241 °C. IR (KBr): $\nu_{\text{P=O}}$ = 1199 s cm^{-1} . ¹H-NMR (CDCl₃): δ 7.96–7.86 and 7.56–7.50 (m, 20H, P(O)Ph₂), 7.06 (s, 4H, *m*-ArH), 6.33 (s, 4H, *m*-ArH), 4.56 (d, 4H, OCH₂P(O)Ph₂, ²*J*_{PH} = 4 Hz), 4.21 and 3.06 (AB spin system, 8H, ArCH₂Ar, ²*J* = 13 Hz), 3.31 (s, 6H, OCH₃), 1.33 (s, 18H, Bu^t), 0.77 (s, 18H, Bu^t). ¹³C{¹H}-NMR (CDCl₃): δ 155.63–124.52 (aromatic C), 71.82 (d, OCH₂P(O)Ph₂, *J*_{PC} = 84 Hz), 60.26 (s, OCH₃), 34.06 and 33.49 (2s, C(CH₃)₃), 31.67 and 31.00 (2s, C(CH₃)₃), 31.46 (s, ArCH₂Ar). ³¹P{¹H}-NMR (CDCl₃): δ + 24.3 (s, P(O)Ph₂). *Anal. Calc.* for C₇₂H₈₂O₆P₂ (*M_r* = 1105.40): C, 78.23; H, 7.48. *Found:* C, 77.94; H, 7.64.

2.3. COMPLEXATION OF SILVER BY **1**

AgBF₄ (0.017 g, 0.088 mmol) was added to a solution of **1** (0.100 g, 0.08 mmol) in CH₂Cl₂ (10 mL). After 24 h, the solution was filtered and concentrated and pentane was added, affording a white precipitate (0.080 g, 70%). *Anal. Calcd.* for C₈₂H₁₀₀AgBF₄N₂O₈P₂ (*M_r* = 1498.34): C, 65.73; H, 6.73; N, 1.87. *Found:* C, 65.50; H, 6.67; N, 1.82. MS (FAB), *m/z* (%): 1411.5 (73) [M – BF₄]⁺. IR (KBr): $\nu_{\text{C=O}}$ = 1623 s cm^{-1} . For NMR, see Table III.

2.4. EXTRACTION

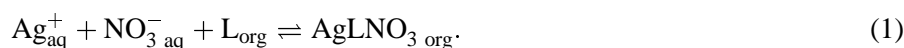
Liquid–liquid extraction experiments were performed in a stoppered glass tube immersed in a thermostatted water bath (25 °C) using equal volumes (10 mL) of aqueous and organic phase. The aqueous phase contained silver nitrate in the presence of excess copper nitrate (0.5 M). The copper cation was chosen since this metal is relevant to the recovery of electronic industry waste [14]. The extraction equilibrium was reached after 20 minutes under continuous magnetic stirring. The organic phase was centrifuged to complete the separation of phases before the organic phase was stripped with 0.1 M nitric acid. Silver ions present in the two phases were analysed using the flame atomic absorption method (Perkin Elmer 2380). This method was also used for quantitative detection of copper but it was found that such extraction was negligible under these experimental conditions.

2.5. TRANSPORT

The instrumentation used for the transport experiments has previously been described [9, 15–17]. It consists of a thermostatted double layer glass cell (25 °C) into which a glass bell cylinder is inserted so as to separate the inner aqueous receiving phase (phase II = 60 mL) from the outer aqueous feed phase (phase I = 1000 mL). A 7×10^{-4} M solution of **1** or DC18C6 in dichloromethane was used as membrane phase (200 mL). The feed phase was circulated between the cell and a container by means of a peristaltic pump (Ismatec VG-ME). A synchronous motor (Heidolph 2000) provided constant rotation of the cylinder around its axis. A static mixer, immersed in both the membrane and aqueous phase, ensured a rapid homogenization of solute concentrations in the two phases.

3. Results and Discussion

Assuming 1 : 1 stoichiometry for the complexes formed between Ag^+ and each ligand (L), the equation describing the extraction equilibrium of silver nitrate is as follows:



The corresponding concentration extraction constant is then defined as:

$$K_{\text{ex}} = \frac{[\text{AgLNO}_3]_{\text{org}}}{[\text{Ag}^+]_{\text{aq}}[\text{NO}_3^-]_{\text{aq}}[\text{L}]_{\text{org}}} \quad (2)$$

Since dissociation of AgNO_3 may be nearly complete [9], the following expression should be considered:

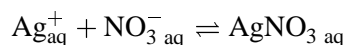


Table I. Logarithm of the extraction equilibrium (K_{app}) of silver nitrate in the presence of an excess of copper nitrate (0.5 M) by **1**, **2**, **3**, **4** and DC18C6 in dichloromethane at 25°C.

Ligand	1	2	3	4	DC18C6
$\log K_{app}$	2.62(±0.02)	1.32(±0.04)	1.64(±0.04)	1.06(±0.04)	1.33(±0.01)

$$\beta = \frac{[\text{AgNO}_3]_{\text{aq}}}{[\text{Ag}^+]_{\text{aq}}[\text{NO}_3^-]_{\text{aq}}}$$

$$[\text{Ag}]_{\text{aq}} = [\text{AgNO}_3]_{\text{aq}} + [\text{Ag}^+]_{\text{aq}} = \beta[\text{Ag}^+]_{\text{aq}}[\text{NO}_3^-]_{\text{aq}} + [\text{Ag}^+]_{\text{aq}}$$

$$[\text{Ag}^+]_{\text{aq}} = \frac{[\text{Ag}]_{\text{aq}}}{(1 + \beta[\text{NO}_3^-]_{\text{aq}})} \div \text{or } \propto [\text{Ag}]_{\text{aq}} \text{ (because } [\text{NO}_3^-]_{\text{aq}} \text{ is constant)}$$

then, it seems appropriate to replace $[\text{Ag}^+]_{\text{aq}}$ by $[\text{Ag}]_{\text{aq}}$ (i.e., the total concentration of silver in the aqueous phase) in Equation (2):

$$K_{app} = \frac{[\text{AgLNO}_3]_{\text{org}}}{[\text{Ag}]_{\text{aq}}[\text{NO}_3^-]_{\text{aq}}[\text{L}]_{\text{org}}} = \frac{[\text{Ag}]_{\text{org}}}{[\text{Ag}]_{\text{aq}}[\text{NO}_3^-]_{\text{aq}}[\text{L}]_{\text{org}}}. \quad (3)$$

Introducing the distribution ratio ($D = [\text{Ag}]_{\text{org}}/[\text{Ag}]_{\text{aq}}$) and subsequent use of logarithms results in the following expression for D :

$$\log D = \log K_{app} + \log[\text{NO}_3^-]_{\text{aq}} + \log[\text{L}]_{\text{org}}. \quad (4)$$

Under the experimental conditions used ($[\text{NO}_3^-]_{\text{aq}} = 1 \text{ M} \gg [\text{Ag}]_{\text{aq}}$), Equation (4) can be rewritten:

$$\log D = \log K_{app} + \log[\text{L}]_{\text{org}}. \quad (5)$$

Plots of $\log D$ vs. $\log[\text{L}]_{\text{org}}$ for ligands **1**, **2**, **3**, **4**, and DC18C6 (Figure 2) are linear with slope near unity, thereby confirming the 1 : 1 stoichiometry of the extracted species in the organic phase.

The corresponding K_{app} values (Table I) reveal the following order for the relative extractive properties of the ligands :

$$\mathbf{1} > \mathbf{3} > \text{DC18C6} \approx \mathbf{2} > \mathbf{4}.$$

In order to compare the extraction properties of macrocyclic ligands for a given cation, one should consider the role of several factors, such as electronic effects, number and types of binding sites, lipophilicity of ligands and cavity size.

The more efficient extractive properties of ligand **1**, with respect to **2**, **3**, **4** and DC18C6, towards silver nitrate might be related to the high basicity of the amide groups [18], the large number of oxygen atoms available for complexation, and

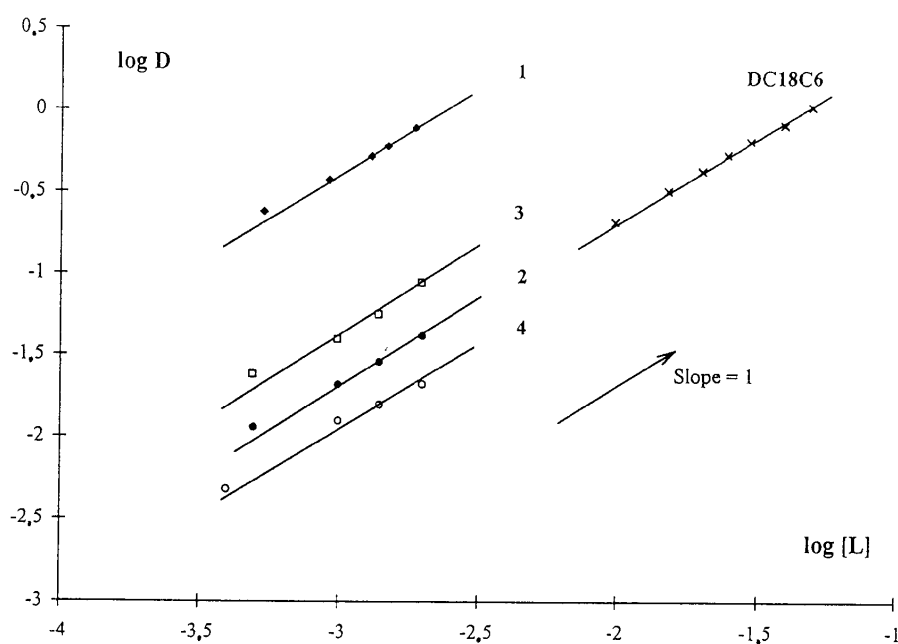


Figure 2. Log D vs. Log $[L]_{\text{org}}$ plot of the extraction of silver nitrate in the presence of copper nitrate (0.5 M) by **1**, **2**, **3**, **4** and DC18C6 in dichloromethane at 25°C.

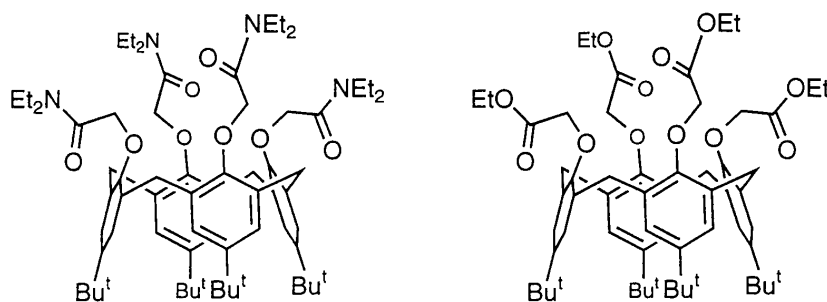


Figure 3. Homo tetra-functionalized calix[4]arene for which silver complex stability constants have been reported (Ref. 19).

(probably) a better matching of the cavity generated by the four pendant arms with the silver cation.

Stability constants for the silver complexes formed with these various ligands are not available. However, data were reported for the related tetra-amide and tetra-ester (Figure 3), showing unambiguously the high complexing power of amido vs. ester functions [19]. Hence, the higher extractive properties of **1** vs. **4** can be explained in terms of the more potent amide- Ag^+ binding.

Note that the relative efficacy of **1** vs. **2** towards extraction of silver nitrate contrasts with the behavior found for the extraction of uranyl and rare earth ions by these same ligands [20].

The reason why **3** displays better extractive properties than **2** may be due to the fact that **3** is less sterically crowded, leading to improved flexibility of the ligand and, therefore, to a more optimized matching of guest and host.

The higher extractive power of **2** vs. **4** is in keeping with the realization that phosphoryl groups have higher polarity than C=O (ester) bonds.

Extraction data are often analysed by considering the distribution isotherm of the extracted solute, defined here as

$$[\text{Ag}]_{\text{org}} = f[\text{Ag}]_{\text{aq}}.$$

Introducing the mass balance equation into Equation (3) gives

$$[\text{L}]_{0, \text{org}} = [\text{L}]_{\text{org}} + [\text{Ag}]_{\text{org}}$$

while the expression for the distribution isotherm is:

$$[\text{Ag}]_{\text{org}} = K_{\text{app}}[\text{NO}_3^-]_{\text{aq}}[\text{L}]_{0, \text{org}} \frac{[\text{Ag}]_{\text{aq}}}{1 + K_{\text{app}}[\text{NO}_3^-]_{\text{aq}}[\text{Ag}]_{\text{aq}}}. \quad (6)$$

This latter expression can be simplified

$$\frac{[\text{Ag}]_{\text{org}}}{[\text{L}]_{0, \text{org}}} = K_{\text{app}} \frac{[\text{Ag}]_{\text{aq}}}{1 + K_{\text{app}}[\text{Ag}]_{\text{aq}}} \quad (7)$$

within the experimental conditions: $[\text{NO}_3^-]_{\text{aq}} = 1 \text{ M} \gg [\text{Ag}]_{\text{aq}}$.

Confirmation of the validity of the assumed equilibrium is readily obtained by considering the following function

$$\frac{[\text{Ag}]_{\text{org}}}{[\text{L}]_{0, \text{org}}} = f([\text{Ag}]_{\text{aq}}),$$

which is independent of the total ligand concentration (Figure 4). The observed slight discrepancy from idealized behavior observed for **1** at higher concentrations of silver or ligand is attributed to the onset of a solubility limit for the extracted complex. The K_{app} values deduced by application of Equation (7) are 385 (± 30) and 50 (± 5) for **1** and DC18C6 [9], respectively. These values are in good agreement with those reported in Table I considering experimental errors.

The kinetics of the transport process were measured by plotting the silver concentration in each of the three phases vs. time for both **1** and DC18C6 (Figure 5). These time-dependent changes were analysed by assuming diffusion through the stagnant films (Figure 6) and by applying the two-film theory to the bulk-liquid membrane [9, 17].

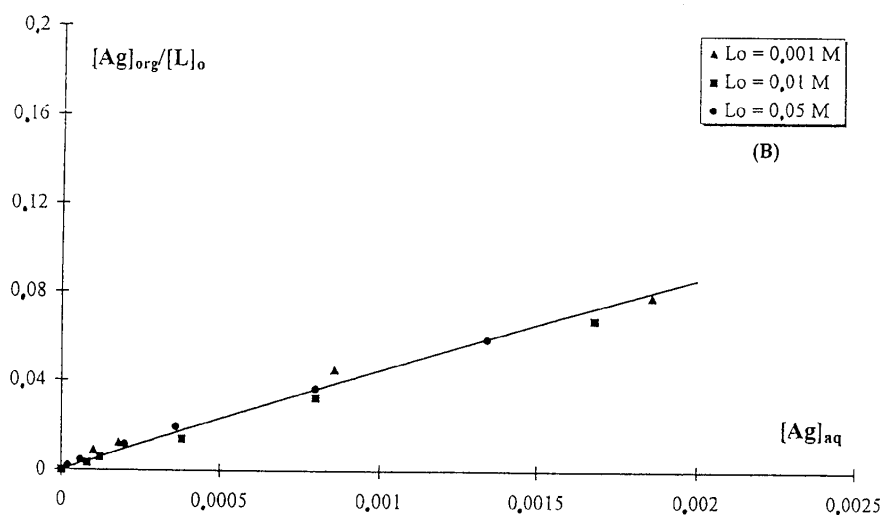
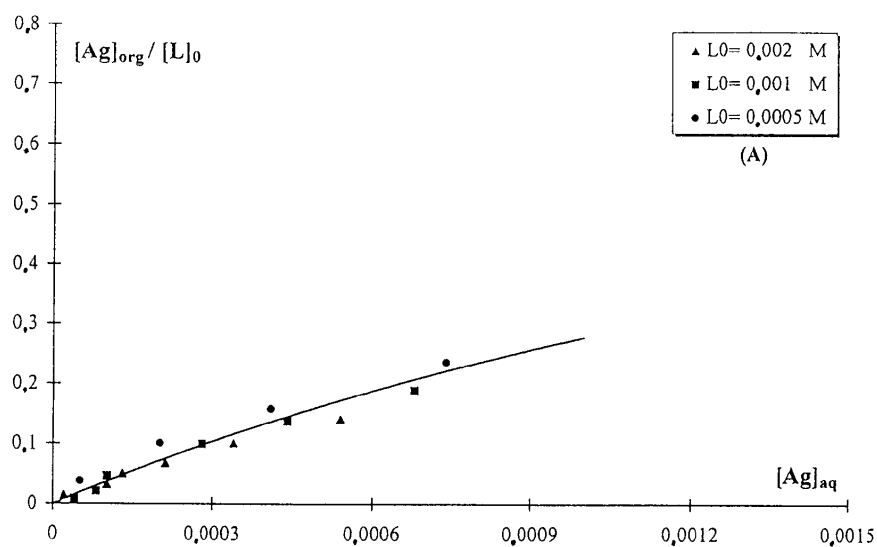


Figure 4. Distribution isotherm of silver nitrate between a 0.5 M copper nitrate solution and a dichloromethane solution of **1** (A) and DC18C6 (B) at 25°C.

According to this model, Equation (7) provides the necessary relationship that links the first interface equilibrium concentrations:

$$[\text{Ag}]_{\text{org } i1} = K_{\text{app}}[\text{L}]_{0, i} \frac{[\text{Ag}]_{\text{aq } i1}}{1 + K_{\text{app}}[\text{Ag}]_{\text{aq } i1}} \quad (8)$$

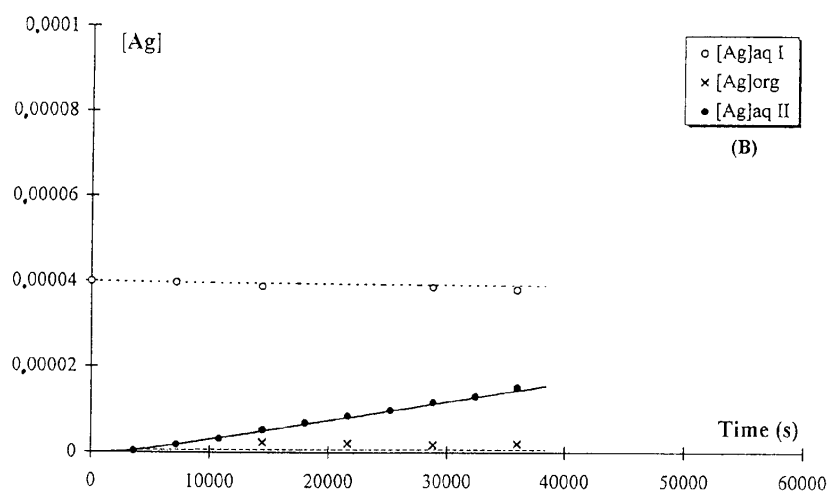
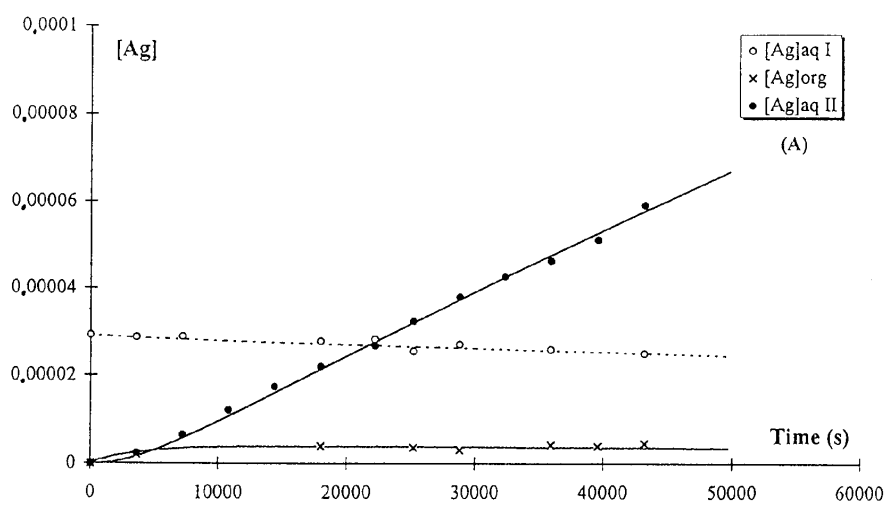


Figure 5. Evolution of the silver nitrate concentration in the receiving, membrane and feed phases as a function of time using **I** (A) and DC18C6 (B) as carriers at 25°C. The conditions are the same as those mentioned in the footnote of Table II.

provided $[L]_0 = [L]_{0,i}$.

It can be shown that, under the experimental conditions used, the $[Ag]_{org, i2}$ concentration is zero at all times. This expectation is supported by the experimental data of the distribution of silver nitrate in the absence of copper nitrate (Figure 7).

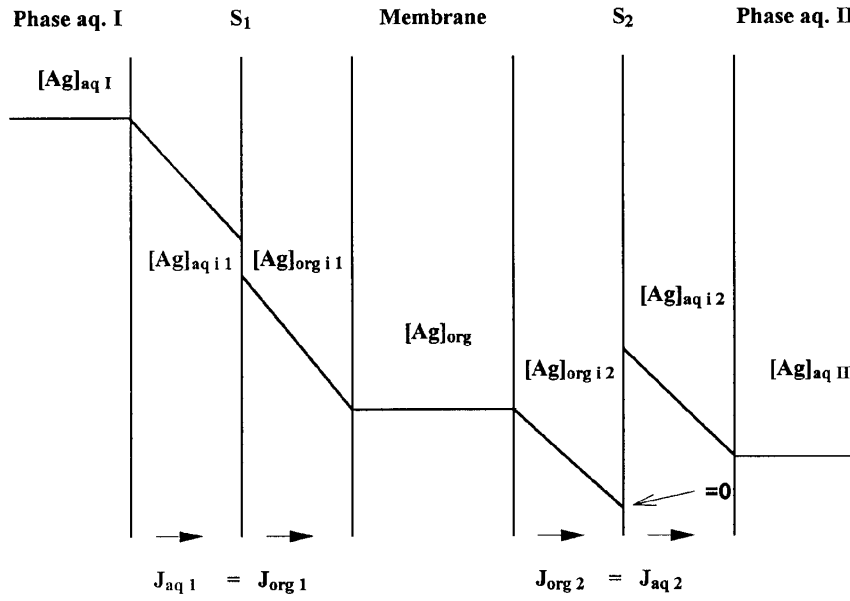


Figure 6. Silver concentration profile across the bulk liquid membrane.

The flux equations for the stagnant films are as follows (Figure 6, see also the nomenclature):

$$J_{aq\ 1} = \frac{V_{aq\ I}}{S_1} \frac{d([Ag]_{aq\ I})}{dt} = k_{aq\ 1} ([Ag]_{aq\ I} - [Ag]_{aq\ i\ 1})$$

$$J_{org\ 1} = k_{org\ 1} ([Ag]_{org\ i\ 1} - [Ag]_{org})$$

$$J_{org\ 2} = k_{org\ 2} ([Ag]_{org} - [Ag]_{org\ i\ 2}) = k_{org\ 2} [Ag]_{org}$$

$$J_{aq\ 2} = \frac{V_{aq\ II}}{S_2} \frac{d([Ag]_{aq\ II})}{dt} = k_{aq\ 2} ([Ag]_{aq\ i\ 2} - [Ag]_{aq\ II}).$$

Assuming equal fluxes for the adjacent stagnant films:

$$J_{aq\ 1} = J_{org\ 1}; \quad J_{org\ 2} = J_{aq\ 2}; \quad S_1 \cdot J_{aq\ 1} - S_2 \cdot J_{aq\ 2} = V_{org} \frac{d([Ag]_{org})}{dt}$$

the following mass balance equation for silver becomes:

$$V_{aq\ I} [Ag]_{aq\ I} + V_{aq\ II} [Ag]_{aq\ II} + V_m [Ag]_{org} = V_{aq\ I} [Ag]_0$$

with the following boundary conditions:

$$t = 0, \quad [Ag]_{aq\ I} = [Ag]_0; \quad [Ag]_{org} = 0; \quad [Ag]_{aq\ II} = 0.$$

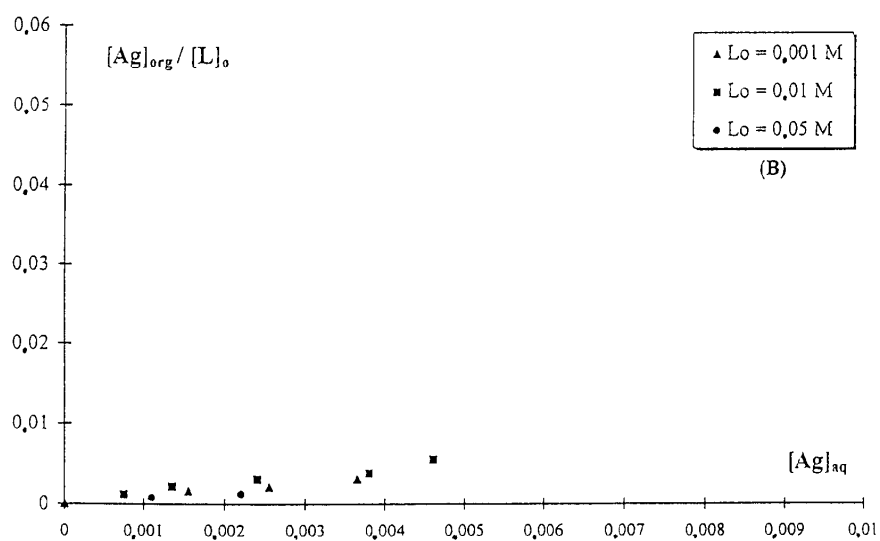
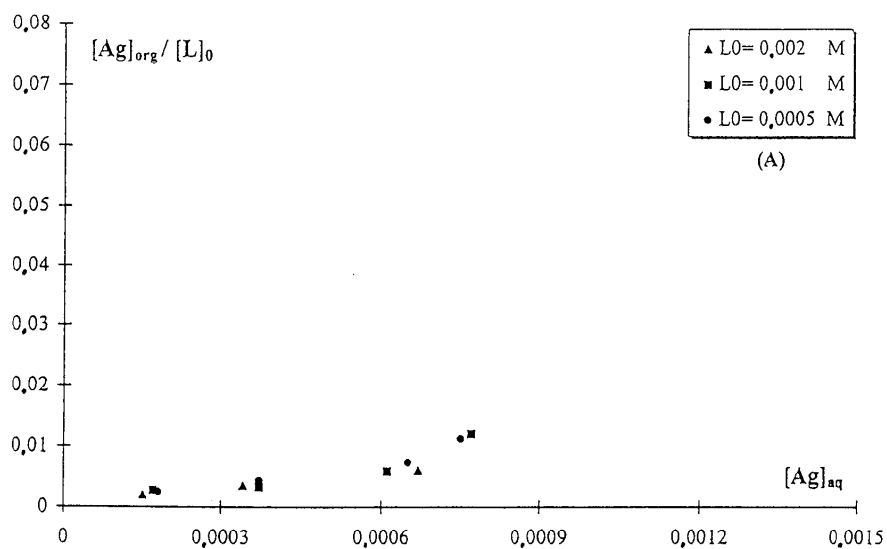


Figure 7. Distribution of silver nitrate between distilled water and a dichloromethane solution of **1** (A) and DC187C6 (B) at 25°C.

This model was tested by comparing calculated curves with the corresponding experimental data (Figure 5) and by introducing the appropriate values of k_1 and k_2 (Table II). It is seen that both theoretical and experimental data reach steady

Table II. Transport rates and evaluated coefficients of transfer at feed (k_1) and receiving (k_2) interfaces at 25°C.^a

Ligand	k_1^b	k_2^b	V_s^c
1	1.47×10^{-4}	1.23×10^{-4}	5.40×10^{-6}
DC18C6	1.95×10^{-4}	1.62×10^{-4}	1.62×10^{-6}

^aMembrane phase: 7×10^{-4} M of ligand in dichloromethane, feed phase: 3×10^{-5} and 4×10^{-5} M AgNO₃ (for **1** and DC18C6 respectively) and 0.5 M Cu(NO₃)₂, receiving phase: water, stirring: 150 cycles min⁻¹.

^bCoefficient of transfer at the feed (k_1) and receiving (k_2) phase in dm s⁻¹.

^cTransport rate at pseudo-steady state (mol L⁻¹ h⁻¹).

state at $t > 5000$ seconds. The corresponding rate V_s (Table II) was found to be ca. 3 times higher for **1** relative to DC18C6.

It should be noted that the k value observed for the DC18C6–AgNO₃ system is higher than that found for the **1**–AgNO₃ system within the proposed model. This disparity is attributed to the difference in the diffusion coefficients of transported species. Considering the same diluent (dichloromethane) in the two systems, the difference of coefficient transfer and diffusion coefficient arise from the size of the migrating species, as already observed in the transport processes of alkali cations by **1**, **2** and DC18C6 [8]. The smaller DC18C6 complex has a higher diffusion coefficient [21] and thereby a larger transfer coefficient. As a result, it is seen that transfer through a liquid membrane by large-sized macrocyclic carriers is influenced by the size of the migrating species.

Proton NMR spectra recorded at 25°C were run in order to obtain insight into the way in which ligand **1** binds silver (I) (Table III). The spectrum of the complex indicates a C_2 -symmetrical structure, as found earlier for the [K ⊂ **1**]⁺ complex [8]. Participation of the phenolic oxygen atoms in cation binding appears very likely in view of the observed downfield shift of the *m*-ArH hydrogen atoms upon complexation [22]. The results are consistent with those reported for sodium and potassium complexation by **1** [8]. Furthermore, complexation of Ag⁺ by the phosphoryl groups is probable, considering the downfield shift of the ³¹P-NMR signal ($\Delta\delta = +7$ ppm). The IR spectrum (KBr or Nujol) shows an intense absorption peak centered at ca. 1623 cm⁻¹ (free ligand, 1658 cm⁻¹), indicating coordination of the amide groups. These results suggest full encapsulation of the silver ion inside the cavity defined by the four lower rim substituents and is reminiscent of the results for a tetraketone-calix[4]arene reported by Ohto *et al.* [7]. It is noteworthy that the solutions containing [Ag ⊂ **1**]⁺ are stable during prolonged storage.

Table III. ^1H -NMR chemical shifts (ppm) of selected signals of ligand **1** and its complex with AgBF_4 .

Proton	Ligand	Complex	$\Delta\delta^a$
H_A^b	4.78	4.28	-0.50
H_B^c	2.86	2.98	0.12
<i>m</i> -ArH	6.39	6.86	0.47
	6.63	7.26	0.63
$-\text{CH}_2\text{CON}(\text{Et})_2$	4.63	4.47	-0.16
$-\text{CH}_2\text{P}(\text{O})\text{Ph}_2$	5.94	5.22	-0.72

^a $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{free ligand}}$.^bAxial ArCH_2 hydrogen atom.^cEquatorial ArCH_2 hydrogen atom.

4. Conclusion

The ability of the multi-oxygen donor **1** to form a highly stable $[\text{Ag} \subset \mathbf{1}]^+$ complex contrasts with the results obtained previously with other calixarene-derived ligands, in particular those allowing aromatic π -bonding to Ag^+ or Reinholdt's calixspherands. The reported NMR and IR data clearly support a structure having an encapsulated silver(I) ion located inside the ionophore cavity of the ligand. Compound **1** displays high extractive properties for silver and enables in particular removal of trace amounts of silver even in the presence of a large excess of copper. The high extractive properties of the diamide-di(phosphine oxide) derivative used in this study confirm the crucial role played by the amide groups in the complexation of silver(I) ions. The good extractive properties of **1** parallel the results obtained in transport experiments with this ligand.

5. Nomenclature

[Ag]	Silver concentration (M)	aq	Aqueous phase
[L]	Ligand concentration (M)	org	Organic phase
<i>S</i>	Interface area (dm^2)	I	Feed aqueous bulk
<i>V</i>	Phase volume (L)	II	Receiving aqueous bulk
V_s	Pseudo-steady state rate ($\text{mol L}^{-1} \text{h}^{-1}$)	<i>i</i>	At interface
<i>t</i>	Time (s)	1	Feed/membrane interface
<i>J</i>	Silver flux ($\text{mol s}^{-1} \text{dm}^{-2}$)	2	Receiving/membrane interface
<i>k</i>	mass transfer coefficient (dm s^{-1})	0	Initial concentration

Acknowledgment

One of us (M.R. Y.) thanks the Ministry of Culture and Higher Education (M.C.H.E.) of Iran and the Société Française d'Exportation des Ressources Educatives (S.F.E.R.E.) for their support. We are grateful to Prof. A. Harriman for an inter-

esting discussion. We are greatly indebted to Dr. Loeber for supplying a synthetic procedure for compound **3**.

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