

Ligand Field Effects on the Transport of 3d Metal Ions across a Bulk Liquid Membrane by Lipophilic Tetraamine Carriers

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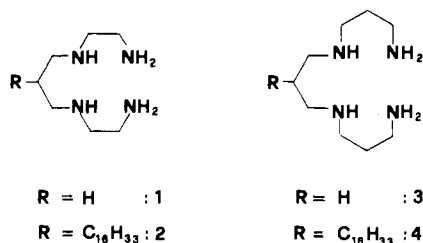
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The two lipophilic tetraamines 6-hexadecyl-1,4,8,11-tetraazaundecane (**2**) and 7-hexadecyl-1,5,9,13-tetraazatridecane (**4**) have been synthesized and used as carriers for the transport of metal ions across liquid membranes. Extraction experiments from aqueous solutions of MX_2 ($\text{M} = \text{Ni}, \text{Cu}, \text{Zn}$) to a CH_2Cl_2 layer containing **2** or **4** have been preliminarily carried out. The metal is extracted in the organic phase as the MLX_2 species ($\text{L} = \text{2 or 4}$), and in particular (i) copper is extracted to a larger extent than nickel and zinc, and because of the competition of the H^+ and M^{2+} ions for the tetraamine, the process is pH controlled and (ii) the copper extraction yield is fairly dependent upon the nature of the inorganic anion X^- , decreasing in the order $\text{Br}^- > \text{Cl}^- > \text{ClO}_3^- > \text{NO}_3^- > \text{ClO}_4^-$, a parallel sequence to the ligating tendencies of the axially bound counterions. Transport experiments, performed by interfacing two aqueous layers by a bulk CH_2Cl_2 membrane, made 5×10^{-4} M in the tetraamine carrier **2** or **4**, and driven by a metal concentration gradient, showed that Cu^{II} is selectively transported in the presence of equimolar amounts of Ni^{II} and Zn^{II} ions. Selectivity is strongly enhanced by the use of **2** rather than **4** as carrier. This seems to be ascribed to the ability of the donor set of **2** to establish strong interactions with those metal ions that, like copper(II), strongly profit from a tetragonal coordination.

Introduction

There has been a growing interest over the past 10 years in the transport of metal ions across artificial membranes. Most of the work has been concerned with alkaline and alkaline-earth cations, and transport studies have been parallel with the development of multidentate carriers containing oxygen donor atoms, in particular crown ethers¹ and cryptands.² In contrast, much less attention has been devoted to the transport processes involving transition-metal ions, in spite of the fact that d-block coordination chemistry is a sound and well-established area of research and hundreds of ligands with selective coordinating properties have been made available in the past few decades.

In this work we describe the design and use of carriers for the transport of divalent ions of the first d transition series, namely Ni^{II} , Cu^{II} , and Zn^{II} . In particular, the two lipophilic tetraamines **2** and **4** have been synthesized and employed as carriers. Classical



solution chemistry studies have previously shown that the parent molecules **1** and **3** can bind Ni^{II} , Cu^{II} , and Zn^{II} and that the different structures of the amines strongly affect the solution stability of the metal complexes.³⁻⁸

The purpose of this work is to assess to what extent a variation of the coordinating properties of carriers of similar nature may affect the selectivity in the transport of ions across membranes. Neutral carriers of the type investigated here can transport metal ions (in particular Cu^{II}) with simultaneous transport of anions according to a process controlled by a concentration gradient. We

have recently described the specific transport of Cu^{II} , mediated by a diamine-diamide macrocycle, driven by a pH gradient.⁹

Experimental Section

Syntheses of the Ligands. The synthetic route to the carrier molecules **2** and **4** investigated in this work is outlined in Scheme I.

Diethyl 2-Cetylmalonate (5). A 4.6-g portion of sodium metal (0.2 mol) was dissolved under nitrogen in 500 mL of absolute ethanol. To the warm (50 °C) solution was added 32 g of diethyl malonate (0.2 mol) dropwise, followed by 61.2 g (0.2 mol) of cetyl bromide. The solution was stirred for a further 15 h and then concentrated at reduced pressure until a pale yellow residue was left. The residue was taken up in hot CHCl_3 , the white precipitate of NaBr was filtered off, and the solution was dried over Na_2SO_4 . The chloroform was then removed on a rotary evaporator, leaving a yellow oil, which was fractionated under vacuum: yield 47 g (61%); bp 195–200 °C (0.5 torr).

6-Cetyl-1,4,8,11-tetraazaundecane-5,7-dione (6). An 8.5-g portion of **5** (0.022 mol) was added dropwise at room temperature to 80 mL of ethylenediamine. The reaction mixture was stirred for 3 days; after a few hours a white precipitate started forming. The precipitate was collected by filtration, washed with water and ethyl acetate to remove unreacted ethylenediamine and ester, and dried under vacuum: yield 7.4 g (81%); mp 130–132 °C.

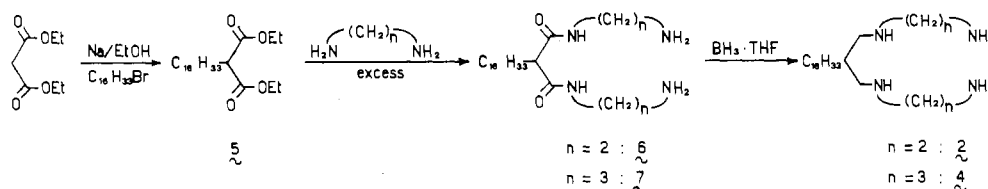
7-Cetyl-1,5,9,13-tetraazatridecane-6,8-dione (7). **7** was obtained with a similar procedure from **5** (10 g) and 1,3-diaminopropane (100 mL): yield 10.6 g (92%); mp 136–138 °C.

6-Cetyl-1,4,8,11-tetraazaundecane (2). A 5-g portion of **6** (0.012 mol) was dissolved under nitrogen in 250 mL of anhydrous THF; to the solution was added 80 mL of 1 M $\text{BH}_3 \cdot \text{THF}$ solution in THF (Aldrich), and the mixture was heated to reflux. After 7 h a further 80 mL of $\text{BH}_3 \cdot \text{THF}$ solution was added and refluxing was continued overnight. The solution was allowed to cool, and 100 mL of methanol was added to destroy unreacted BH_3 ; the mixture was then evaporated to dryness at reduced pressure. The residue was treated with a mixture of water (40 mL), methanol (100 mL), and 37% HCl (25 mL) and refluxed for about 1 h. The solution was evaporated to dryness and the solid residue treated with 100 mL of 5 M NaOH solution. A layer of whitish granules formed on the surface of the solution. The solid was collected by filtration and dissolved in CH_2Cl_2 while the mother liquor was extracted with three 50-mL portions of CH_2Cl_2 . The combined extracts (250 mL) were dried over Na_2SO_4 and then evaporated to dryness, leaving a waxy

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- (12) Due to the scarcity and, in some cases, unreliability of hydration free energy exchange data for the investigated anions and cations, we prefer to use enthalpy data. Discussion is based on the assumption that the hydration entropy term does not vary too seriously along the investigated series of anions.

Scheme I

**Table I.** Anion Effects on the Extraction of Cu^{2+} as CuLX_2 in a CH_2Cl_2 Layer Containing the Lipophilic Tetraamine L (L = 2, 4)

X^-	$\Delta H_{\text{h}}^{\circ}(\text{X}^-)^c$	carrier 2 ^a		carrier 4 ^b	
		$R\%d$	$\nu_{\text{d-d}}e$	$R\%d$	$\nu_{\text{d-d}}e$
Br^-	-347	40	14 120	47	14 300
Cl^-	-381	36	15 060	42	14 760
ClO_3^-	-348	33	17 360	42	16 070
NO_3^-	-314	32	17 860	40	15 700
ClO_4^-	-229	32	17 980	36	16 780

^aAfter equilibration of 10 mL of CH_2Cl_2 , 5×10^{-4} M in 2, with 10 mL of an aqueous solution 5×10^{-4} M in CuSO_4 and 0.05 M in NaX .¹⁰ ^bAfter equilibration of 10 mL of CH_2Cl_2 10^{-3} M in 4 with 10 mL of an aqueous solution 10^{-3} M in CuSO_4 and 0.1 M in NaX .¹⁰ ^cHydration enthalpies (kJ mol^{-1}), from ref 11.¹² ^dExtraction yield for copper; uncertainty $\pm 2\%$. ^eFrequency of the maximum of the absorption band of the CuLX_2 chromophore in CH_2Cl_2 solution (cm^{-1}).

material, which was dried under vacuum: yield 1.9 g (40%); mp 98–100 °C. Anal. Calcd for $\text{C}_{23}\text{H}_{32}\text{N}_4$: C, 71.81; H, 13.62; N, 14.56. Found: C, 71.56; H, 13.52; N, 14.41.

7-Cetyl-1,5,9,13-tetraazatridecane (4). 4 was obtained with a similar procedure by reduction of the corresponding diamide 7 (3 g) with $\text{BH}_3 \cdot \text{THF}$ (150 mL of a 1 M solution in THF): yield 1.8 g (64%); mp 96–98 °C. Anal. Calcd for $\text{C}_{25}\text{H}_{36}\text{N}_4$: C, 72.75; H, 13.68; N, 13.57. Found: C, 72.38; H, 13.51; N, 13.42.

The reduction of the diamino diamides to the corresponding tetraamines was demonstrated by the disappearance of the amide $\text{C}=\text{O}$ stretching band (1680 cm^{-1}).

Extraction Experiments. Extraction experiments were typically performed by equilibrating 10 mL of a 5×10^{-4} M aqueous solution of the MX_2 metal salt (if necessary made 5×10^{-2} M in a NaX electrolyte and adjusted at the desired pH value with standard HClO_4 or NaOH) with 10 mL of a 5×10^{-4} M solution of the lipophilic tetraamine 2 or 4 in CH_2Cl_2 . To make the equilibration faster, the flasks containing the biphasic systems were stirred for 2 h on an electromechanical oscillating stirrer. The extraction yield, $R\%$, was determined by measuring the amount of the metal ion in the aqueous layer before and after the extraction. The reported $R\%$ values are the average of at least three determinations and are affected by an uncertainty lower than 3%.

Transport Experiments. The cell used for the transport experiments was a cylindrical glass beaker (8 cm height, 4 cm diameter), divided into two vertical compartments by a vertical glass plate, except for the bottom portion (1.5 cm). The liquid membrane (30 mL of a CH_2Cl_2 solution of 2 or 4) was located at the bottom of the glass beaker. Atop the organic phase were carefully placed the aqueous phases (10 mL each), which were separated from each other by the glass plate. The cell was sealed with Parafilm, to minimize evaporation. The organic layer was magnetically stirred (200 rpm) by a Teflon-coated bar (18 mm \times 5 mm diameter). In the course of the transport experiment, samples of both aqueous phases were analyzed for metal content by atomic absorption spectroscopy.

Physical Measurements. pH measurements on the aqueous layers in both extraction and transport experiments were performed by using a combined glass electrode with a Radiometer PHM 80 pH meter. Spectra of the CH_2Cl_2 layers were measured on a Cary 2300 UV-VIS-near-IR apparatus using 10-mm cells. AAS analyses were performed on an IL model 551 spectrophotometer.

Results

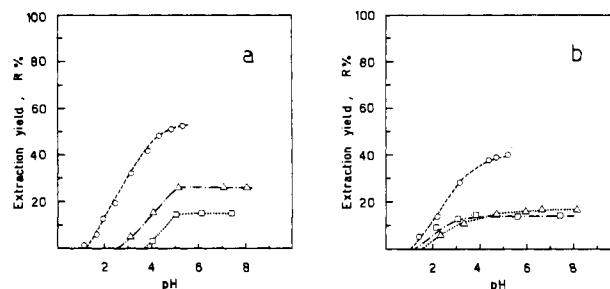
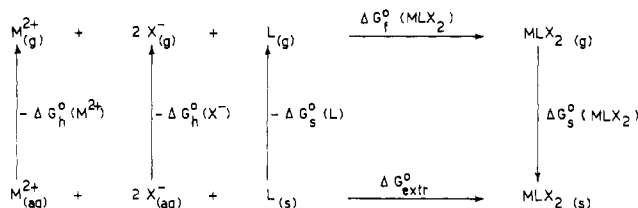
The results of the extraction experiments (extraction yields, $R\%$, and related parameters) are reported in Tables I and II. Extraction yields for a given metal have been found to be affected (i) by the pH of the aqueous layer and (ii) by the nature of the anion X^- .

The effect of the acidity of the aqueous source solution is shown in Figure 1: in particular, when the pH of the solution is increased, the extraction yield steeply increases until it reaches a constant

Table II. Extraction of Metal $\text{M}(\text{ClO}_4)_2$ Salts (M = Ni, Cu, Zn) from an Aqueous Layer to a CH_2Cl_2 Layer Containing a Lipophilic Tetraamine L (L = 2, 4)^a

M^{2+}	$\Delta H_{\text{h}}^{\circ}(\text{M}^{2+})a$	L = 2		L = 4	
		$R\%b$	$K_{\text{E}}c$	$R\%b$	$K_{\text{E}}c$
Ni^{2+}	-2105	27	9.3	17	8.9
Cu^{2+}	-2100	53	10.3	40	9.8
Zn^{2+}	-2046	15	8.8	14	8.8

^aHydration enthalpies (kJ mol^{-1}) from ref 11.¹² ^bLimiting values taken from Figure 1. ^c K_{E} , extraction coefficient, $= [\text{MLX}_2] / ([\text{M}^{2+}(\text{aq})][\text{X}^-(\text{aq})]^2[\text{L}(\text{CH}_2\text{Cl}_2)])$.

**Figure 1.** Effect of the pH on the extraction yield, $R\%$, of $\text{M}(\text{ClO}_4)_2$ salts from an aqueous layer (10 mL, 5×10^{-4} M) to a CH_2Cl_2 layer containing (a) 2 or (b) 4 (10 mL, 5×10^{-4} M): (O) M = Cu; (Δ) M = Ni; (\square) M = Zn.**Figure 2.** Thermodynamic cycle associated with the extraction of an MX_2 metal salt (e.g. $\text{Cu}(\text{ClO}_4)_2$) from an aqueous layer to an organic layer containing a complexing agent L (e.g. 2 or 4).

value. This qualitatively indicates that both H^+ and M^{2+} ions compete for the tetraamine: when protonated, the tetraamine cannot bind the metal ion and there is a pH value at the beginning of the "plateau" in Figure 1 at which the competition by the hydrogen ions does not occur any longer. It can also be seen from Figure 1 that, for a given tetraamine, the extraction yield decreases in the order $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$. Moreover, in the case of copper, in order to evaluate the effect of the nature of the anion X^- , extraction experiments have also been performed with use of aqueous layers containing a 100-fold excess of NaX . $R\%$ values, reported in Table I, decrease in the order $\text{Br}^- > \text{Cl}^- > \text{ClO}_3^- > \text{NO}_3^- > \text{ClO}_4^-$, for both tetraamines investigated.

Discussion

Molecules 2 and 4 have been designed with the general requirements that an extracting agent (or carrier) should fulfill kept in mind. In particular, (i) a multidentate ligand framework has been chosen to allow the formation of fairly stable 1:1 complexes (due to the chelate effect), according to an uncomplicated mechanism, (ii) the process of formation of the metal/carrier complex at the aqueous source phase/organic layer membrane interface (as well as the demetalation process at the membrane/receiving phase interface, in the transport experiments) is

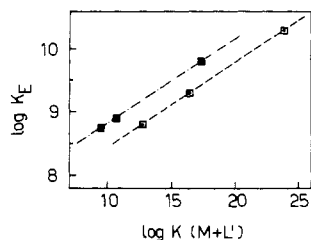


Figure 3. Correlation between the extraction coefficient, K_E , for the process $M^{2+}(aq) + 2X^-(aq) + L(CH_2Cl_2) = MLX_2(CH_2Cl_2)$ and the complexation constant, $K(M + L')$, for the equilibrium $M^{2+}(aq) + L'(aq) = ML'^{2+}(aq)$: (□) $L = 2$, $L' = 1$; (■) $L = 4$, $L' = 3$.

sufficiently fast, due to the open nature of the molecules, and (iii) the presence of a long aliphatic chain appended to the ligand backbone guarantees solubility in the organic layer and complete insolubility in the aqueous layer.

The results of the extraction experiments can be interpreted on the basis of the thermodynamic cycle reported in Figure 2. From this cycle, the free energy change associated to the water-to-dichloromethane metal extraction, ΔG°_{extr} , can be expressed as the algebraical sum of the following five energy contributions:

$$\Delta G^\circ_{extr} = -\Delta G^\circ_h(M^{2+}) - 2 \Delta G^\circ_h(X^-) - \Delta G^\circ_s(L) + \Delta G^\circ_f(MLX_2) + \Delta G^\circ_s(MLX_2) \quad (1)$$

where the subscript h indicates hydration (gas-to-water) terms, the subscript s indicates solvation (gas-to-dichloromethane) terms, and $\Delta G^\circ_f(MLX_2)$ is the free energy term associated with the formation of the MLX_2 complex in the gas phase.

Let us first consider the extraction of an $M(ClO_4)_2$ salt by the lipophilic tetraamine. The following sequence of extraction yields $R\%$ is observed: $Cu^{2+} > Ni^{2+} > Zn^{2+}$. It should be noted that in these circumstances the $\Delta G^\circ_h(X^-)$ and $\Delta G^\circ_s(L)$ terms in eq 1 are the same. Moreover, the $\Delta G^\circ_s(MLX_2)$ term can be reasonably considered to be constant along the series of the investigated metals. Therefore, the ΔG°_{extr} value, which is related to the extraction coefficient K_E according to the equation $\Delta G^\circ_{extr} = -RT \ln K_E$, should result from the balance of the gas-phase complexation term $\Delta G^\circ_f(MLX_2)$ and the metal hydration term $\Delta G^\circ_h(M^{2+})$. The hydration enthalpies of the investigated metal ions, reported in Table II, do not seem to correlate well with the extraction data. On the other hand, the evaluation of $\Delta G^\circ_f(MLX_2)$ is not straightforward, but one can reasonably consider that it should be proportional to the $\log K$ values associated with the complexation process in aqueous solution ($M(aq) + L'(aq) \rightleftharpoons ML'(aq)$), where L' represents the parent hydrophilic unsubstituted tetraamines 1 or 3.⁷ Figure 3 shows that a direct correlation exists between $\log K_E$ and $\log K(M + L')$ for the tetraamines 2 and 4. This indicates that the determining contribution to the extraction process is the complexation energy term, which predominates over the metal ion dehydration term.

A second approach keeps the metal constant and considers the effect of the variation of the nature of the carrier. Limiting $R\%$ values in Table II (and in Figure 3) show that, in the case of Ni^{II} and Cu^{II} ions, the tetraamine 2 extracts much more metal than the longer tetraamine 4. In contrast, for the case of Zn^{II} , extraction yields are the same for both carriers. Figure 2 shows that, for a given metal, ΔG°_{extr} results from the balance of the complexation energy in the gas phase ($\Delta G^\circ_f(MLX_2)$) and the "solvation terms" (desolvation of L , $-\Delta G^\circ_s(L)$, and solvation of MLX_2 , $\Delta G^\circ_s(MLX_2)$), in the CH_2Cl_2 layer. It seems reasonable to assume that the $\Delta G^\circ_s(MLX_2) - \Delta G^\circ_s(L)$ difference is constant for the two investigated tetraamines. Thus, the extraction yield should be strictly related to the ability of the extracting agent to establish strong coordinative interactions with the metal ion. In this connection, it should be noted that previous investigations on the hydrophilic analogues of the tetraamines here considered have shown that 1 (2,3,2-tet, the parent ligand of 2) has the appropriate dimensions and structure to chelate divalent metal ions, according to a square-coplanar coordinating mode in a strain-free config-

uration, and to establish strong in-plane M-N interactions:⁷ in contrast, 3 (3,3,3-tet, the parent ligand of 4) is too large and, because of steric constraints, gives much less intense coordinative interactions in the equatorial plane.⁶ Accordingly, the 3d cations Ni^{II} and Cu^{II} , which prefer tetragonal arrangements, strongly profit from the strain-free coplanar coordination offered by 2, compared to the coordination in the sterically disfavored tetraamine 4. In contrast, the Zn^{II} ion, having a d^{10} configuration, is not as much selective with respect to the coordination geometry and does not discriminate between the two tetraamines of different size 2 and 4.

Furthermore, a moderate anion effect exists in the copper extraction, $R\%$ values decreasing along the series $Br^- > Cl^- > ClO_3^-$, $NO_3^- > ClO_4^-$ for both investigated tetraamines. From the thermodynamic cycle in Figure 2, it can be deduced that the extraction process results from the energy balance of the anion dehydration term $\Delta G^\circ_h(X^-)$ and the gas-phase complexation term $\Delta G^\circ_f(MLX_2)$. In particular, for a given tetraamine, the complexation term is mainly related to the formation of more or less strong M-X coordinative bonds.

Inspection of values in Table II indicates that no direct relationship exists between $\Delta G^\circ_h(X^-)$ and extraction yields. On the other hand, $CuLX_2$ species are expected to exhibit, in CH_2Cl_2 solution, the typical distorted-octahedral stereochemistry shown by copper tetraamine complexes, with the ligand spanning the four equatorial sites and with the two X^- anions occupying the apical positions. It has been shown that for a $Cu^{II}N_4X_2$ chromophore (where N represents the coordinated amine group), the intensity of the axial Cu-X interactions is inversely proportional to the energy of the copper d-d absorption band.¹³ The ν_{d-d} values of $CuLX_2$ complexes in dichloromethane are reported in Table I. It should be noted that the sequence of the extraction yields $R\%$ appears to be inversely related to the sequence of ν_{d-d} values. This may indicate that the Cu-X energy term predominates in the extraction process and, in particular, strong axial interactions (e.g. those exerted by the Br^- anion) favor the transfer of Cu^{2+} from water to dichloromethane (compared to the case for the more weakly coordinating ClO_4^- anion).

On the other hand, it should be considered that in the extraction of alkali-metal cations, with crown ethers used as ligands, the yield decreases along the series $ClO_4^- > I^- > NO_3^- > Br^- > Cl^-$,¹⁴ which parallels the sequence of the dehydration energy of X^- . The different behavior seems to be ascribed to the fact that the complexed alkali-metal cation interacts with X^- through a simple electrostatic mechanism (ion pair) and no direct M-X interaction occurs, in contrast to the situation observed with the copper tetraamine complexes investigated here.

Selective Transport of Cu(II) across a Bulk CH_2Cl_2 Membrane. The two-phase (extraction) process described before can be considered as a preliminary step to the three-phase (transport) process. The latter experiment presents many advantages compared to the extraction, with special reference to the selective separation of metal ions. The relationship between transport and extraction selectivities has been thoroughly discussed in a recent paper by Lehn and co-workers.¹⁵

Transport studies have been carried out by interfacing two aqueous phases (the source phase, SP, containing the metal ion to be transported and the receiving phase, RP) with a stirred layer of CH_2Cl_2 , made 5×10^{-4} M in the carrier molecule, 2 or 4. SP and RP differed only in the presence of the 3d metal ion (e.g. Cu^{II}), dissolved as the perchlorate, and were both made 0.1 M in $NaClO_4$. Again, the poorly coordinating ClO_4^- anion has been chosen in order to minimize the M-X interaction effects. The pHs of SP and RP were adjusted at the value corresponding to the "beginning plateau" of the pH-dependent extraction experiments (see Figure 1), i.e. the minimum pH value at which the competition of hydrogen ions for the tetraamine carrier disappears. In order to guarantee stable conditions during the long time of the ex-

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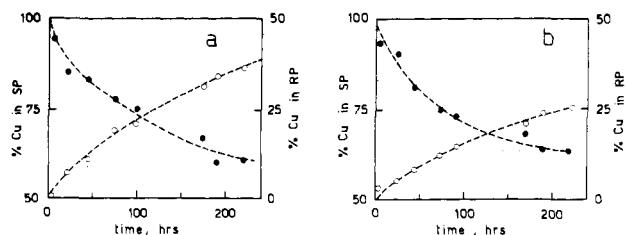


Figure 4. Transport of Cu^{II} by lipophilic tetraamines vs. time: (a) carrier 2; (b) carrier 4. Full circles refer to the metal content (%) in the source phase (SP) and correspond to the scale on the left of each figure. Open circles refer to the metal content (%) in the receiving phase (RP) and correspond to the scale on the right.

periments (up to 220 h), the pH was adjusted with a buffer (0.1 M phthalate), rather than with standard HClO₄, as done in extraction experiments. It is obvious that the presence in the aqueous layer of the phthalate ion, which weakly coordinates Cu^{II} ions,¹⁶ alters the conditions with respect to the extraction studies.¹⁷

At the beginning of the experiment the liquid membrane turns blue-violet, due to the formation of the metal-carrier complex CuL(ClO₄)₂. In the following hours, a blue color appears in the RP, due to the formation of the copper(II)-phthalate complex, whereas the intensity of the blue color of the SP weakens. The driving force of the described transport process is the concentration gradient of the metal ion and is expected to lead to an equilibrium situation in which the concentration of Cu²⁺ is the same in both SP and RP. The decrease of the concentration of Cu²⁺ in SP and the corresponding increase in RP was monitored by analyzing, through AA spectroscopy, samples taken from SP and RP at selected time intervals: corresponding data are shown in parts a and b of Figure 4 for the transport experiments with carriers 2 and 4, respectively.

When experiments were stopped, after 220 h, copper contents in the aqueous receiving layer (expressed as the percentage of the amount placed in the SP at the beginning of the experiment) were the following: experiment with carrier 2, 37%; experiment with carrier 4, 25%. These results indicate that 2 represents a much more efficient carrier for the transport of copper across liquid membranes, compared to 4.

Lehn¹⁵ has recently elucidated the relationship existing between the transport rate (three-phase process) and the extraction coefficient K_E (two-phase process): at not too high K_E values, the transport rate values parallel the trend of the extraction coefficients. However, in the case of the formation of very stable

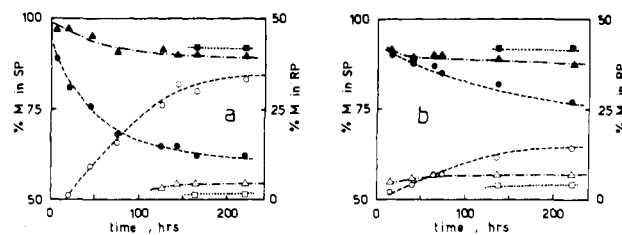


Figure 5. Multiple transport of Cu^{II}, Ni^{II}, and Zn^{II} ions by the lipophilic tetraamines vs. time (Cu^{II} (O), Ni^{II} (Δ), Zn^{II} (□)): (a) carrier 2; (b) carrier 4. Full symbols refer to the metal content (%) in the source phase (SP) and correspond to the scale on the left of each figure. Open symbols refer to the metal content (%) in the receiving phase (RP) and correspond to the scale on the right.

metal-carrier complexes (very high K_E values), the opposite behavior occurs, and the higher extraction coefficients make the transport rates lower. Our experiments seem to fall in the former situation: the metal-carrier complexes are stable enough to guarantee extraction, but not so stable as to cause a slow metal release into the receiving phase. Thus the results of the transport experiments parallel those of the extraction processes.

In order to test the selectivity of the systems under investigation, studies of multiple transport of metal ions were carried out by placing in the SP equimolar amounts of Ni²⁺, Cu²⁺, and Zn²⁺. The pH and supporting electrolyte concentrations were the same as described for the transport of the sole copper ion. The results of the multiple-transport experiments are shown in Figure 5. The figure shows that the three metal ions are simultaneously transported by carriers 2 (Figure 5a) and 4 (Figure 5b), but transport of copper occurs at a remarkably greater rate. In order to assess the selectivity effects in the multiple transport, we consider as a useful parameter the amount of metal transported after a given time (e.g. 220 h). The corresponding percentage values are defined as R_{220} . Selectivity in the transport of copper(II) by a carrier compared to the transport of another metal ion also present can be expressed by the ratio of the R_{220} values. $R_{220}(\text{Cu}^{\text{II}})/R_{220}(\text{Ni}^{\text{II}})$ is 8 in the case of carrier 2 and 2 for carrier 4; on the other hand, $R_{220}(\text{Cu}^{\text{II}})/R_{220}(\text{Zn}^{\text{II}})$ is 33 for 2 and 4 for 4. This indicates that 2 is an excellent carrier for the selective transport of Cu^{II} in the presence of Ni^{II} and Zn^{II} ions, whereas 4 presents much less discriminating transport properties. In this case too, transport selectivity parallels the extraction selectivity, in particular reflecting the enhanced coordinating tendencies of 2 toward metal ions which, as Cu(II), can strongly profit from ligand field stabilization effects.

Registry No. 2, 104051-53-8; 4, 104051-54-9; 5, 41433-81-2; 6, 104051-55-0; 7, 104051-56-1; Cu, 7440-50-8; Ni, 7440-02-0; Zn, 7440-66-6; Br⁻, 24959-67-9; Cl⁻, 16887-00-6; ClO₃⁻, 14866-68-3; NO₃⁻, 14797-55-8; ClO₄⁻, 14797-73-0.

(16) Graddon, D. P. *J. Inorg. Nucl. Chem.* **1958**, *5*, 219.

(17) Extraction experiments have shown that the phthalate ion is not extracted as its copper salt in a CH₂Cl₂ layer containing 2 or 4. Thus the phthalate ion should not be involved in the transport as a counterion.