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Solvent Extraction and Related Studies on Silver Recovery from Aqueous Solutions

A. P. Paiva[a]
[a] CECUL (INIC) RUA DA ESCOLA POLITÉCNICA, LISBON, PORTUGAL

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REVIEW

Solvent Extraction and Related Studies on Silver Recovery from Aqueous Solutions

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A. P. PAIVA
CECUL (INIC)
RUA DA ESCOLA POLITÉCNICA
58-1200 LISBON, PORTUGAL

Abstract

The main research in the solvent extraction of silver is exhaustively reviewed, together with relevant data on the metal ion complexation properties in one phase. Such features as the transport of competitive cations through liquid membranes and selectivity in silver extraction are also reviewed. The behavior of organic ligands interacting with silver is analyzed on the basis of the atom type or types directly responsible for extraction/complexation processes.

1. INTRODUCTION

Solvent extraction is widely used in metallurgical processing. Although it is increasingly used in industrial applications, there is a significant gap between the technique as an operating process and the associated scientific knowledge.

The main purpose of this review is to contribute to the clarification of the chemical processes involved in the solvent extraction of silver. The importance of this work arises because of the precious metals content in the majority of the world's basic metal ores which are or can be recovered by solvent extraction. Therefore, this bibliographic research describes investigations regarding the complexation of silver in one phase, the solvent extraction of this metal, and its transport properties. It summarizes the most relevant background information needed to develop a better comprehension of the chemical reactions between the interacting species.

Some researchers (*1–4*) have recently suggested that the overall phenomenon inherent in the solvent extraction of metals cannot be understood without considering the physicochemical aspects related to the existence of two phases. Thus, the role of the liquid–liquid interface, including such phenomena as diffusion, mass transfer, and kinetics of the interacting species, has almost been forgotten in research regarding the solvent extraction process.

As a result, all the papers referred to in this review consider the chemistry involved in the process to be occurring in the bulk phases, either aqueous or organic. Future studies concerning the extraction mechanisms of metals will probably be focused on the liquid–liquid interface.

2. BRIEF INTRODUCTION TO SOLVENT EXTRACTION METHOD

The solvent extraction process (or liquid–liquid extraction), as used in extractive metallurgy, is presented in a very simplified way in Fig. 2.1 (*5*).

In the extraction stage the extractable metal, which is contained in the aqueous phase, is transferred from the aqueous to the organic phase (solvent: extractant plus diluent) by the selective extractant. The loaded solvent is then mixed with a suitable aqueous phase, and the metal is transferred from the organic to the aqueous solution—the stripping phase. This phase usually has a fair concentration of the metal salt, so it can be processed by electrowinning to produce the metal in its final form.

Solvent extraction is always an equilibrium process; thus, to have a measure of the equilibrium achieved after the aqueous and organic phases are shaken, the concentrations of metal in the aqueous solution before and after extraction can be analyzed. The difference between the two measured concentrations gives the metal concentration in the organic phase. Therefore, for a particular set of experimental conditions, solvent extraction can be defined by an extraction coefficient, *D*, which is the ratio between the

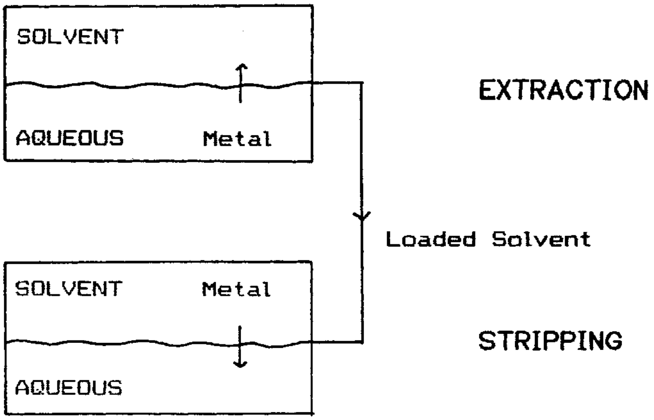


FIG. 2.1. Solvent extraction process.

total metal concentration in whatever form in the organic phase and the total metal concentration in whatever form in the aqueous phase after extraction (*1*).

$$D = [\text{metal}]_o/[\text{metal}]_a \tag{1}$$

The coefficient D is a basic parameter that is frequently calculated in solvent extraction studies. An extraction can be considered effective if it gives a value of D better than 0.5.

Although there are a few ways of classifying solvent extraction systems, the one based on the nature of the reaction involved in the extraction process is convenient (*6*). Thus, the following types can be classified.

i) Extraction by Physical Distribution. This is the least frequently used system of all the metallurgical extraction systems. A simple molecular distribution of the solute between the aqueous phase—where it is scarcely solvated—and an inert solvent is the only feature involved. A typical example is the extraction of ruthenium tetroxide into a solvent such as carbon tetrachloride (*6*).

ii) Extraction by Solvation. This system involves the replacement of some or all of the coordinated water molecules of a metal cation by the molecules of the extractant, forming species which are soluble in the organic phase. The majority of the extractants of this type are oxygen-containing molecules such as ethers, ketones, and neutral organophosphorus compounds (*6*).

iii) Extraction by Anion Exchange. In this kind of extraction, anionic metal species are extracted in the form of ion pairs with a suitable cation contained in the organic phase following the exchange of a nonmetallic anion between the two phases. The organic cations are usually protonated amine or phosphine bases (*6*).

iv) Extraction by Cation Exchange. This system arises when the extracted metal cation forms an electrically neutral coordination complex with the extractant by displacing another cation, usually a proton. When a proton exchange takes place, the extractability shows a significant dependence on the pH value of the aqueous phase. $\text{pH}_{0.5}$ is an important coefficient for the given metal, i.e., the pH value at which the concentrations of the metal are equal in both phases at the same stated concentration of extractant (*6*).

This classification does not mean that a given extractant *has* to belong to a particular extraction system; it depends greatly on the experimental conditions adopted for the extraction (*5*).

It is also important to note that most of the available data related to solvent extraction is empirical in nature, consequence of the complexity of the mechanisms involved. Up to now, the opportunities for understanding or predicting the behavior of such systems have been scarce.

3. LIQUID–LIQUID EXTRACTANTS OF SILVER

The ligands used for the complexation and solvent extraction of silver are of three types:

- Open-chain ligands (or noncyclic)
- Macrocyclic ligands
- Polycyclic cryptands

Their differences are shown schematically in Fig. 3.1.

3.1. Open-Chain Ligands

As there are several ligands which have been tested as complexants and/or extractants of silver, it seems reasonable to analyze them on the basis of the atom type directly implicated in the process.

3.1.1. With Oxygen Atoms

There are not many recent studies regarding the interactions between the silver ion and open-chain ligands with oxygen atoms. This fact is a result of the knowledge that there is not a great affinity between silver ion—a "soft" acid—and the oxygen atoms—"hard" bases. Nevertheless,

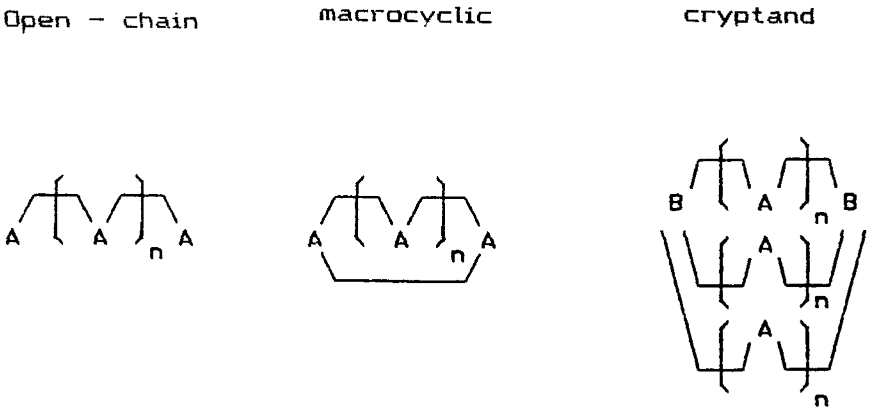
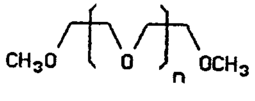


FIG. 3.1. Types of ligands (open-chain, macrocyclic, cryptand).

TABLE 3.1.1.1
Silver Complexation with the Ligands Indicated (silver nitrate in ammonium perchlorate solution, methanol, 25°C)

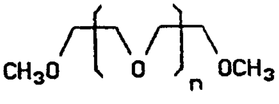
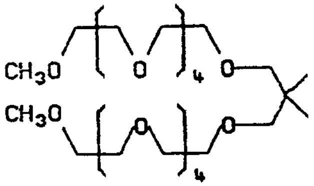
Ligands	log K
	
n = 3	too small
n = 4	1.80
n = 5	1.82

Buschmann measured the formation constants of some silver complexes of this type (Table 3.1.1.1) (*7*).

For this particular set of experimental conditions, the complexes formed are very weak.

Another study regarding this type of ligand shows that the extraction of silver ion from a picrate medium by an organic phase of dichloromethane containing some oxygen ligands is not efficient (*8*) (Table 3.1.1.2).

TABLE 3.1.1.2
Extraction Studies of Silver Ion by the Ligands Indicated (25°C)

Ligands	Extraction (%)
	
n = 3	0.1
n = 4	0.5
	1.2

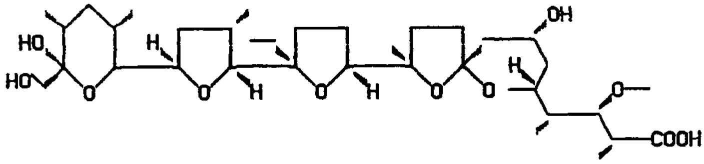


FIG. 3.1.1.1. Structure of monensin.

Cox and coworkers (*9*) were attracted by the reported good results in terms of cation transport in biological membranes shown by the natural product monensin (Fig. 3.1.1.1). They measured the stability constant of the silver complex and found a value of log K_s (25°C, M^{-1}, ethanol) of about 8.94. Recently, Tsukube and Sohmiya (*10*) found that the methyl ester of the monensin molecule significantly enhanced transport selectivity and efficiency for the silver ion (see Section 3.5).

A Japanese patent of 1988 for the manufacture of silver powder (*11*) uses a solvent extraction process. As the organic phase, Takagi (*11*) used a naphtenic acid (the sort of compound often found in petroleum, where it is the simplest 1-methyl-cyclopentane-carboxylic acid) dissolved in kerosine.

In general, the oxa-alkanes do not seem good and selective extractants for silver ion.

3.1.2. With Sulfur Atoms

In the 1970s and the first years of the 1980s, some papers by USSR researchers appeared involving the extraction of silver by petroleum derivatives containing organic sulfur (*12*). The authors claimed that the extraction efficiencies obtained were generally greater than those found with hexyl and/or octyl sulfides.

A solvent extraction study using hexyl sulfide reports that this ligand extracts Ag^+ from a 1-M nitric acid solution for a molten diphenyl organic phase at 70°C (*13*)—D = 25.9—but extraction with the same ligand in 1,2-dichloroethane is not efficient after equilibration with a 1% silver nitrate aqueous solution containing ammonium acetate and sodium perchlorate (*14*). Therefore, these results show that experimental conditions for extraction play an important role in the process.

Another type of sulfur ligand is presented in Table 3.1.2.1 (*14*).

The diluent influence on extraction efficiency is remarkable. A lack of understanding sometimes exists for the extractant/complex/diluent interactions.

A review of the coordination chemistry of thio-, seleno-, and telluroethers (*15*) reports some properties of Ag^+ complexes, including li-

TABLE 3.1.2.1
Silver Extraction with 1,2-Bis-(hexylthio)ethane (aqueous phase: silver nitrate 0.2 mM, ammonium acetate 0.1 M, sodium perchlorate 10 mM, 25°C)

Ligand	Diluent	Extraction (%)
 (5 mM)	1,2-dichloroethane	100
	Toluene	5

gands, such as dialkyl and diaryl thioethers, bidentate thioethers of the $RS(CH_2)_nSR$ (n = 2–5) type, together with the types *cis*-R′—SCH=CHS—R′ and *o*-C_6H_4—$(SCH_3)_2$. The monodentate ligands generally form 1:1 complexes; the latter tend to form 1:2 complexes involving a tetrahedral Ag^+ (*15*).

Torgov (*16*) published a review describing the use of extractants such as sulfides and sulfoxides for the separation of noble and nonferrous metals with analytical and hydrometallurgical purposes.

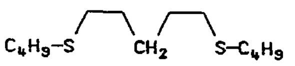
The same author and his collaborators analyzed the extraction capacities of unsaturated organic sulfides toward several metal ions (*17*) by examining the effects of diluent nature and sulfide structure on silver extraction. They reported (*17*) that both 1:1 and 1:2 silver–sulfide complexes are formed, and they concluded that the ability of silver to form π-bonds with alkenyl groups improves the extraction capacities of this type of sulfide toward the metal.

Dietze et al. (*18*) studied the complex formation and the extraction of silver ion by sulfur ligands. They evaluated the stability constants of the complexes formed in dioxane–water (75% v/v) mixtures (see Table 3.1.2.2). The greater stability of the 1:2 complex of ligand 2 over the same type of complex exhibited by the other ligands seems remarkable, and it can be explained by chelate formation of both ligands with 5-membered rings and tetrahedral coordination by sulfur surrounding the silver ion (*18*).

Extraction studies of silver from a nitric medium with the ligands presented in Table 3.1.2.2 show that butyl sulfide and 1,2-(butylthio)-ethane form complexes of the AgL_2^+ kind. A 1:1 complex prevails for the extraction by ligands with a wider spatial separation of the sulfur atoms (*18*). In addition, all the extraction processes are controlled by complex formation and their stabilities for the particular set of experimental conditions in which extraction was carried out.

Sekido and Chayama (*19*) studied the extraction behavior of silver with acyclic tetrathioethers (Fig. 3.1.2.1), and they concluded that the extract-

TABLE 3.1.2.2
Stability Constants of the Silver Complexes with the Ligands Indicated at 25°C

Ligands	log K	
	log K_1(1:1)	log K_2(1:2)
$C_4H_9-S-C_4H_9$	3.1	1.7
	4.6	3.7
	4.3	2.2

ability is larger than that performed by the analogous cyclic tetrathioethers. In fact, the flexibility of these acyclic tetrathioethers seems to be responsible for the improved stability of the silver complexes formed. The compositions and extraction equilibrium constants of the silver complexes with each of the ligands in Fig. 3.1.2.1 are presented in Table 3.1.2.3.

Although little is known about the structure of this type of complex, it can be said that ligands 1) and 2) in Fig. 3.1.2.1 are so flexible that a silver ion can be encircled by one molecule of the ligand (*19*). For the remaining complexes, coordination of silver ion with the four sulfur atoms is not

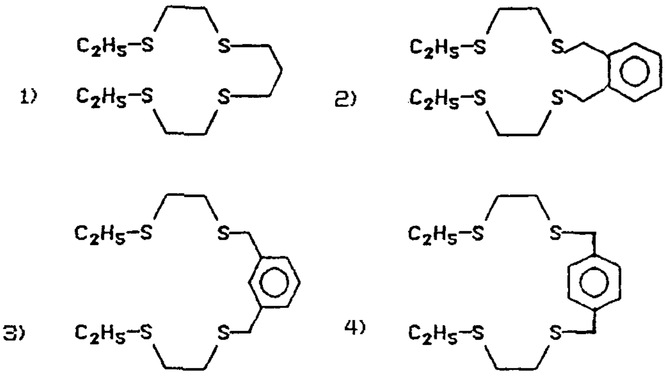


FIG. 3.1.2.1. Acyclic tetrathioethers tested as extractants for silver ion.

TABLE 3.1.2.3
Composition and Extraction Equilibrium Constants of the Silver Complexes (picrate medium, 25°C, ligand L dissolved in 1,2-dichloroethane)

Ligands	Ag:L:Pic	Log K_{ex}
1)	1:1:1	10.4
2)	1:1:1	11.2
3)	1:1:1	10.5
4)	1:1:1	9.3

possible, and therefore a dimeric extracted entity (Ag:L:Pic 2:2:2) seems to occur (*19*).

Syntheses of thia-alkanes are usually easy, and the results reported for their extraction properties toward silver contained in a nitric medium are encouraging. However, it must be pointed out that this type of ligand is not a good one for the extraction of silver from a concentrated chloride medium (*20*), although it is very good for extractions from a sulfuric medium. The different chlorocomplexes of silver which exist in a chloride aqueous phase do neutralize the attraction of the sulfur ligands toward the metal (*20*).

3.1.3. With Phosphorus Atoms

The complexation chemistry of organophosphorus compounds, both neutral and acid, has been extensively investigated, mainly for analytical purposes. These compounds are nowadays commonly used as ligands for the solvent extraction of several metal ions.

For the case of silver, there are some works reporting the extraction of this metal ion by tributylphosphate from a thiocyanate medium (*21*), by a synergistic mixture of bis-(2-ethylhexyl)-phosphoric acid and 4-*sec*-butyl-2-(2-methylbenzyl)-phenol in kerosine at pH 2–3 (*22*), by bis-(2-ethylhexyl)-phosphoric acid from a perchlorate solution (*23*), and by tributylphosphate from hydrochloric acid solutions (*24*) and nitrate solutions (*25*). However, nothing was said regarding the selectivity of extraction in all these studies.

In order to find selective extractants for silver, and accordingly to the principle of hard and soft acids and bases (HSAB) developed by R. Pearson, many authors have prepared and tested various thiophosphorus extractants. These extractants can be divided into two classes: acid and neutral

(*26, 27*). Handley and coworkers (*28, 29*) studied the extraction properties of di-*n*-butyl-phosphorothioic and *O,O'*-di-*n*-butyl-phosphorodithioic acids toward silver and many other metal ions, and concluded that "soft" metal ions such as Ag^+, Hg^{2+}, and Pd^{2+} are efficiently extracted either from hydrochloric acid or sulfuric acid solutions.

However, the selectivity toward silver is not totally reached in the presence of some metal ions such as Cu^{2+} and Zn^{2+}. Besides, the dithiophosphoric acids and the *O,O'*-dialkylphosphoromonothioic acids are susceptible to hydrolysis at temperatures above 30 and 50°C, respectively (*26, 27*).

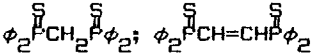
Nevertheless, a more recent study of these types of compounds was carried out by Shong and coworkers (*30*) who remarked on the better behavior of bis-(2-ethylhexyl)-dithiophosphoric acid over the bis-(2-ethylhexyl)-phosphoric acid for the extraction of silver from a nitric medium.

The neutral ligands have been extensively investigated. The related work is summarized in Table 3.1.3.1. Most of these ligands are efficient and selective extractants of Ag^+, Hg^{2+}, and Pd^{2+} from aqueous nitric, sulfuric, or hydrochloric acid solutions. The extractions seem to involve a solvation mechanism, which is typical for this type of ligand (*26, 27*). Organophosphine sulfides (particularly Cyanex 471X), as well as the trialkylthiophosphates, are promising reagents for the selective recovery of silver by a solvent extraction process (*26, 27*). In fact, a technical information sheet regarding the properties of Cyanex 471X points out that this ligand is selective for the extraction of silver and palladium from sulfate, nitrate, and chloride media (*5*).

Triphenylphosphine is another ligand which has been studied for the complexation (*36–41*) and solvent extraction (*14, 42–44*) of silver ion. The reported results show that this is a good ligand of silver nitrate, forming AgL_n^+ complexes (n = 1–4) (*37*). The structures of the complexes $(Ph_3P)_4Ag_4X_4$ (X = Cl, Br, I) and $AgCNS.2Ph_3P$ were established by crystallography (*39, 41*). Interesting work performed by Seeverens et al. (*42*) revealed the excellent properties exhibited by triphenylphosphine as an extractant for silver from hydrochloric acid solutions varying from 1 to 4 M. The ligand was selective for silver in the presence of large concentrations of Cu^{2+}, decreasing with increasing hydrochloric acid concentration. The authors reported additional data concerning the extraction properties of the ligand by using other diluents and different aqueous media. The selectivity for silver showed by this ligand in the presence of a large excess of Cu^{2+} in nitrate medium was remarkable (*44*).

Another interesting study regarding the type of complex formed between the ligand $Ph_2P(CH_2)_2—S—(CH_2)_2PPh_2$ and silver chloride established the structure presented in Fig. 3.1.3.1 (*15*). This study suggests a method for testing the properties of such a ligand as an extractant for silver.

TABLE 3.1.3.1
Main Neutral Thiophosphorus Extractants

	Aqueous Media	References
Tri (alkyl/aryl) thiophosphates		
-Tri-n-butyl-thiophosphate	HNO_3/NO_3^-	(31,32)
-Tri-iso-octyl--thiophosphate	HNO_3/NO_3^-	(31,32)
-O,O′-diiso-propyl--S-benzyl-thiophosphate	HNO_3/H_2SO_4	(13)
-O,O′-dimethyl-O-(3-methyl-4-nitrophenyl)--thiophosphate	HNO_3/H_2SO_4	(13)
-O,O,S-triethyl--dithiophosphate	HNO_3	(34)
-Bismuth bis-(2-ethylhexyl)--dithiophosphate	HCl	(35)
Amides of thiophosphorus acids		
-N,N′,N"-trihexyl-phosphorothioic triamide	HNO_3/H_2SO_4	(33)
Organophosphine sulphides		
-Tri-n-butyl-phosphine sulphide	NO_3^-	(32)
-Triisobutylphosphine sulphide	NO_3^-,SO_4^{2-},Cl^-	(5,26,27)
-Tri-n-octyl-phosphine sulphide	NO_3^-	(32)
Bidentate thiophosphorus extractants		
 $\phi_2\overset{S}{\overset{\parallel}{P}}CH_2\overset{S}{\overset{\parallel}{P}}\phi_2$; $\phi_2\overset{S}{\overset{\parallel}{P}}CH{=}CH\overset{S}{\overset{\parallel}{P}}\phi_2$	$HNO_3/HClO_4$	(26,27)

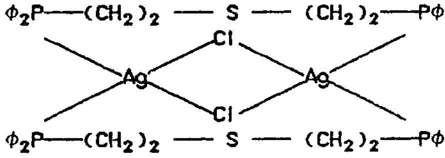


FIG. 3.1.3.1. Structure exhibited by a complex of a thiophosphorus ligand with silver chloride.

A few compounds of this type can be found in commercial routes. Nevertheless, the majority has been obtained by direct synthesis, which frequently is not easy. Although they seem to be promising extractants for silver, these products are often hazardous and poisonous.

3.1.4. With Nitrogen Atoms

The solvent extraction of silver by amines is a process that has already been tested as a result of the existence of several identification studies in analytical chemistry based on the complexation process of these two entities. Therefore, there are a number of papers in the literature regarding the extraction and complexation of silver by amines and ammonium salts (*5, 7, 45*). Amines extract silver from chloride, sulfate, cyanide, and nitrate media, but the efficiency of the process always depends on the acid concentration in the aqueous phase. Nevertheless, it has been shown that silver extraction by amines is more efficient from a chloride (1–2 M in hydrochloric acid) than from a sulfate or nitrate medium (*45*).

Le and coworkers studied the mechanism of silver extraction from a thiosulfate solution by a primary amine which they called (N 1923) nitrate (*46*), and they found that the distribution coefficient *D* decreased with increasing nitrate and thiosulfate concentrations, as well as with pH. The extraction mechanism seems to be an anion-exchange mechanism (*46*).

The selectivity of amines for silver extraction is very poor, although it has been reported that the separation of Ag^+ from Cu^{2+} by trilaurylamine was achieved after adjustment of a suitable set of experimental conditions (*45*).

3.1.5. With Oxygen and Sulfur Atoms

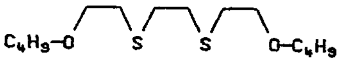
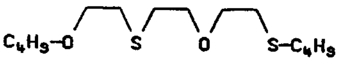
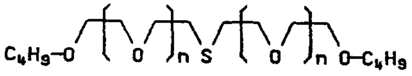
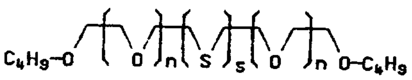
Studies of complexation and solvent extraction involving this type of ligand are less common than the others already reviewed. The idea of using them as extractants for metals, specifically silver, is apparently quite recent.

Complexation studies involving ligands with the structure $S[(CH_2)_nCO_2H]_2$ ($n = 1, 2$) and $HO_2C—CH_2—S—(CH_2)_n—S—CH_2—CO_2H$ ($n = 1, 2$) with silver ion have been carried out and the respective stability constants reported (*47, 48*). Nevertheless, these acids cannot be used as extractants in solvent extraction studies because they are markedly soluble in water.

A group of USSR workers reported some extraction studies using ligands which they called "oxosulfides" (*49*). Nine ketosulfides and four ketobisulfides were tested as extractants for silver. The extraction capacity of octylthiomethylacetophenone is reported to be better than that shown by petroleum sulfides or dialkylsufides (*49*).

As with the analogous sulfur ligands, Dietze and coworkers (*18*) studied the complex formation and extraction properties of some oxathia-alkanes with silver. The stability constants found for the complexes (1,4-dioxane/water, 75% v/v) are shown in Table 3.1.5.1. By comparison with the

TABLE 3.1.5.1
Stability Constants of the Complexes Involving the Ligands Shown and Silver Ion (25°C)

Ligands	log K	
	log K_1 (1:1)	log K_2 (1:2)
1) 	5.7	2.0
2) 	4.7	3.5
3) 	5.6	2.6
4) 	6.6	–
5)  n = 1	3.2	1.7
6) n = 3	3.7	1.2
7)  n = 1	9.0	–
8) n = 2	8.1	–

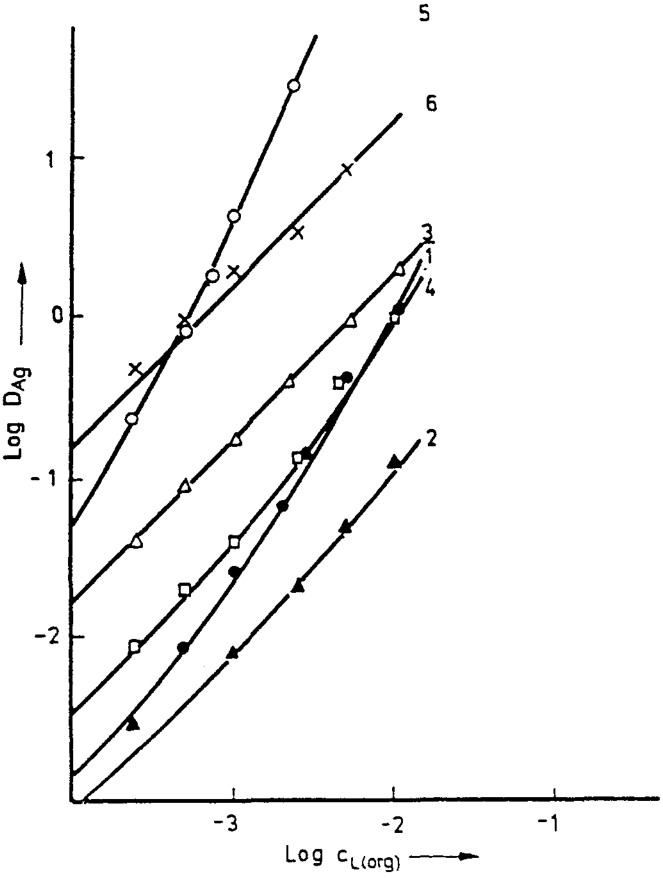
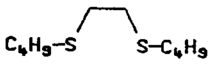
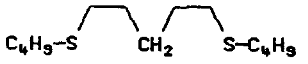
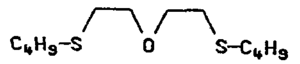
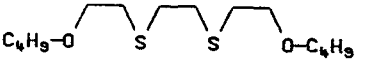
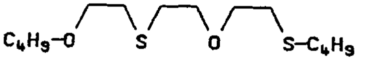


FIG. 3.1.5.1. Extraction of silver with thia- and oxathia-alkanes ($[AgNO_3] = 10^{-4}$ M; $[KNO_3] = 1$ M; $[HNO_3] = 10^{-1}$ M; $[L] = 2.5 \times 10^{-4}$–10^{-2} M/C_6H_6). The ligands are defined in Table 3.1.5.2. Figure reprinted from Reference 18, page 239, by courtesy of Marcel Dekker, Inc.

stability constants of the thia-alkanes (see Table 3.1.2.2), it can be seen that the introduction of oxygen atoms increases the stability of the complexes (*18*). Accordingly, solvent extraction of silver by this type of ligand is more efficient than with the thia-alkanes (Fig. 3.1.5.1), which shows once more that the extraction behavior seems to be primarily controlled by complex formation properties, with the problems of hydrophilic–organophilic distribution playing a minor part (*18*).

Analysis of the former figure and the related extraction equilibrium constants (see Table 3.1.5.2) show that, in general, all the ligands are good

TABLE 3.1.5.2
Extraction Equilibrium Constants of the Thia- and Oxathia-alkanes Studied (22°C, 30 minutes of shaking, benzene)

Ligands	log K	
	log K_{ex1}	log K_{ex2}
1) 	1.1	4.0
2) 	0.9	2.4
3) 	2.1	2.8
4) 	1.5	3.8
5) 	-	6.7
6) 	3.2	-

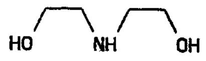
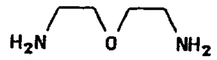
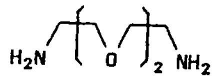
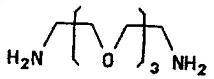
in terms of extraction efficiency. The oxygen atoms, when placed at the center of the molecule, play an important role in increasing the stability/extraction of the complexes due to their coordination with silver ion. Some ligands tend to form 1:2 complexes, others 1:1 complexes, because of the favored spatial geometry obtained in some cases (*18*).

Solvent extraction investigations performed by Dietze and coworkers were carried out for silver in a nitrate medium (*18*); similar oxothia alkanes showed a very poor extraction efficiency toward silver when the metal was included in a chloride medium (*20*) ($[Cl^-] = 5$ M, pH 1), reflecting the inertness of the ligands for interaction with silver in a nonfree state.

3.1.6. With Oxygen and Nitrogen Atoms

There are no solvent extraction studies about metals with this kind of ligand because they are even more soluble in water than amines when in the presence of a strong acidic aqueous phase. Only some complexation

TABLE 3.1.6.1
Stability Constants of the Complexes Formed between the Ligands and Silver Ion (methanol, perchlorate medium 0.05 M)

Ligands	log K
1) 	>5 (10.5 - AgL_3^+)
2) 	7.14
3) 	9.59
4) 	8.55

work involving a few open-chain ligands containing oxygen and nitrogen atoms have been reported (*7*) (Table 3.1.6.1).

The stability of the complex with ligand 2) in Table 3.1.6.1 was also measured in mixtures of acetonitrile and water, and the variation was 5.80 to 7.70 for different proportions of the solvents (*50*).

For a pertinent solvent extraction study using this type of ligand, it would be necessary to obtain secondary amines with long alkyl chains, e.g., from ligands 2), 3), and 4) (see Table 3.1.6.1) or diethers with a similar structure starting from ligand 1). However, this kind of ligand does not seem promising for selective silver extraction, although the complexes formed are usually very stable (*7*).

3.1.7. With Sulfur and Nitrogen Atoms

Compounds included in this section are thiourea and its derivatives. This type of compound is very well known because it exhibits good complexant properties toward several metal salts, which make them widely used for the identification of metals in analytical chemistry.

Therefore, as thiourea derivatives include nitrogen and sulfur atoms, they can be expected to have a reasonable affinity toward silver. There is some work in the literature regarding this type of interaction. Deglev and coworkers (*51*) studied the capacities of diantipyrylthiourea and diphenylthiourea as extractants for some metals in an ammonium aqueous solution, and they concluded that aqueous solutions containng Pb^{2+}, Au^{3+},

Cd^{2+}, Pd^{2+}, Bi^{2+}, Ag^{+}, and Tl^{+} were preconcentrated successfully by extraction of an organic phase of chloroform containing the ligands. Again for analytical purposes, Fishkova et al. (*52*) extracted Ag^{+} by bis-(*o*-tolyl)-thiourea dissolved in butyl acetate, as well as other precious metals.

N,*N*′-Diphenylthiourea was also used as an extractant for silver by Seeverens and coworkers (*42*). Platinum, palladium, silver, and gold are extracted simultaneously by the ligand from hydrochloric acid concentrations ranging from 1 to 4 M when dissolved in dichloroethane. It was also shown that for a low hydrochloric acid concentration (e.g., 1 M), large quantities of copper do not degrade silver extraction when diphenylthiourea is used. The same was true when triphenylphosphine was used, as mentioned before (*42*).

The selectivity exhibited by some 2-alkylthiopyridines as extractants for silver, palladium, and mercury is remarkable (*53*, *54*). In fact, the ligands 2-octylthiopyridine and *t*-dodecylthiopyridine (Fig. 3.1.7.1) extract Pd^{2+} from hydrochloric acid medium faster than sulfur-containing extractants (*53*), and the latter ligand is extremely efficient for the extraction of silver over a large range of nitric acid concentrations (*54*).

Hudson and Shepherd (*55*) used the ligand presented in Fig. 3.1.7.2 and studied its extraction properties toward Au^{3+}, Pd^{2+}, Ag^{+}, Cu^{+}, Cu^{2+}, Pt^{4+}, and Rh^{3+}. The ligand is good for the extraction of Pd^{2+} and Au^{3+} from a strong chloride medium (*55*); they did not supply data for silver extraction. However, the authors made the corresponding silver complex, the elemental analysis and IR spectra established a stoichiometry of 1:1 for it (*55*).

Another complexation study regarding the interaction between silver and some sulfur-containing amino-pyridines was done by Schaubroek and

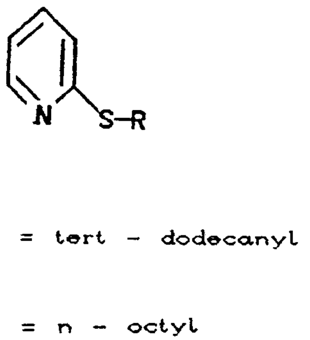


FIG. 3.1.7.1. Ligands for the extraction of silver (toluene–water, nitric medium).

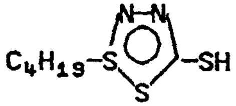


FIG. 3.1.7.2. Ligand for extraction of several metals (water–chloroform, chloride medium).

coworkers (*56*). The authors established the stability constants and the composition of the complexes as a function of pH, as well as the coordination properties of each of them (*56*). This is a group of potentially good ligands for a solvent extraction process for precious metals.

Thioamides of the type R—CS—NHR′ (R, R′ = alkyl, aryl) are also potentially good extractants for silver. Buzlanova et al. (*57*) studied the complexation properties of this type of ligand toward silver nitrate, a method they found for the determination of the ligands by potentiometric titration.

In conclusion, the ligands described in this section can be potentially good extractants for silver in terms of efficiency, provided there is the necessary hidrophobicity of the organic phase. Obviously, the results obtained depend on the composition of the aqueous phase, but the lack of research using hydrochloric acid/chloride solutions is notorious.

For the selective extraction of silver from base metals (mainly Fe^{3+}, Cu^{2+}, and Pb^{2+}), the range of extractants has to be shortened. In fact, taking into account the work already done, the sulfur and sulfur-oxygen ligands for nitric and sulfate media, and the phosphorus and neutral phosphorus-sulfur for the same media and also for chloride media, seem to be the most promising. Although ligands with nitrogen usually form stable complexes with silver, they do not seem to have good selectivity.

A lot of work has to be done in order to clarify the mechanisms of extraction as well as the silver/extractant/diluent interactions. These are not evident in the interpretations of the experimental results published up to now.

3.2. Macrocyclic Ligands

As in the previous section, it seems reasonable to analyze the data available on the complexation/extraction of silver by this type of ligand on the basis of the atoms which are directly implicated in the process.

The easy complexation of metals with crown ethers (namely, the alkaline metals) was deeply evaluated by Pedersen who did the first synthesis of these products in 1967 (*58*). Since then, their syntheses have been greatly developed, and the study of the complexation/extraction properties of crown ethers toward several metal ions is still an active research subject.

The possibility of synthesizing macrocyclic ligands with different heteroatoms has given new perspectives to the complexation and/or extraction of metals which do not exhibit an affinity with oxygen, e.g., silver ion.

From an industrial point of view, application of crown ethers to a solvent extraction process for the recovery of metals does not seem to be a viable process with the present level of knowledge.

3.2.1. With Oxygen Atoms

Takeda did a review of the extraction properties of macrocyclic ligands toward several metal ions in 1984 (*59*). After a theoretical approach, including the equilibria involved in the extraction of metals by this specific type of ligand, the author reported the data of the most significant studies. The extraction constants of the complexes formed for silver and lead ions with some crown ethers (*59*) are presented in Table 3.2.1.1.

Takeda and coworkers (*60*) studied the equilibria involved in the solvent extraction process from water picrate to benzene for silver and thallium systems when using the crown ethers described in Table 3.2.1.1. After a complete mathematical treatment, they concluded that for the two systems in analysis, the relative sizes of the cation and the crown ether cavity, the number of oxygen atoms, and the basicity and the flexibility of the macrocycle are important factors in determining the stabilities of the complexes with the crown ethers studied in benzene solution (*60*).

The extraction equilibrium constants for these same systems (15C5 and 18C6) toward several univalent metal ions show that there are different factors to be considered for each of the crown ethers (*61*). Thus, the sequence of the constants for the 15C5 system depends entirely on the

TABLE 3.2.1.1

Extraction Constants for the 1:1 complexes of Some Crown Ethers with Silver and Lead Ions (picrate medium, water–benzene, 25°C)

Crown – ether	log K_{ex} (Ag^+)	log K_{ex} (Pb^{2+})
12C4	1.96	–
15C5	4.45	6.46
B15C5	3.33	–
18C6	4.44	11.75
DB18C6	3.56	7.16
DB24C8	3.09	6.32

extractability of the univalent metal ion–crown ether complex; for the 18C6 system the sequence depends largely on the stability of the complexes (*61*).

All these systems are difficult to analyze and to rationalize because it is necessary to consider the significant solubility of the crowns in the aqueous phase; Takeda and Takahashi (*62*) carried out the determination of the stability constants of the DB18C6–silver ion complex for benzene and an aqueous solution, and they concluded that the greater stability in the former solution causes the complex to be much more extractable than in the 18C6–silver ion complex (*62*) for the same solvent extraction conditions.

A paper presented by Hasegawa and coworkers (*63*) described the effect of lithium nitrate on the extraction of 15C5, B15C5, 18C6, and DB18C6, and it compared the results with the effect on the extraction of an ion pair consisting of Ag^+/crown ether/picrate anion. The authors concluded that the extractions of the crown ethers were impaired by an increase in lithium salt, as was the extraction of silver. Moreover, in the lower concentration region of lithium salts, silver extraction was affected more markedly than was crown ether itself (*63*).

In more recent work, Takeda and Nishida (*64*) reported a study regarding the solvent extraction of various metal picrates with B18C6 into chloroform. They calculated the extraction equilibrium constants and also considered other equilibria involved (Fig. 3.2.1.1). The authors established that the order of log K_{ex} of B18C6 for the univalent metal ions is $Tl^+ >$

$$K_{ex} = [MLA_m]_o [H^+]^m / [M^{m+}] [L]_o [HA]_o^m \qquad (1)$$

$$K_{D,L} = [L]_o / [L] \qquad (2)$$

$$K_{ex}(HA) = [HA]_o / [H^+] [A^-] \qquad (3)$$

$$K_{M,L} = [ML^{m+}] / [M^{m+}] [L] \qquad (4)$$

$$K_{exio} = [MLA_m]_o / [ML^{m+}] [A^-]^m \qquad (5)$$

FIG. 3.2.1.1. Equilibrium constants for equilibrium between a chloroform solution of a crown ether (L), an aqueous solution of a metal ion (M^{m+}), and a picrate ion (A^-). The subscript "o" indicates the organic phase; and the lack of a subscript indicates the aqueous phase.

$K^+ > Rb^+ > Ag^+ > Cs^+ > Na^+$. Although it has the largest log K_{ML}, B18C6 shows the third lowest extractability for Ag^+. This result is attributed by the authors to the second smallest log $K_{ex,ip}$ value for this metal ion (*64*). Thus, Takeda and Nishida concluded that, for this particular system, the magnitude of K_{ex} is determined largely by the value of $K_{ex,ip}$ (*64*).

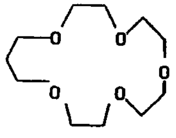
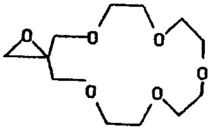
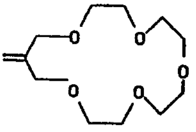
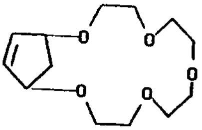
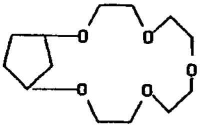
The solvent extraction abilities of 16C5 and its derivatives with single and double lariat side arms at position 15 were extensively investigated by Inoue and coworkers (*8*) toward the alkaline, alkaline-earth, silver, and thallium ions. The authors synthesized all the ligands used and analyzed the results obtained as a function of the substituent effect, the effective donor atoms and steric effects, the single and double side arms, and the lipophilicity of the different crown ethers (*8*). Although the extractabilities of the 16C5 lariats for most mono- and divalent cations increased gradually with an extending oxyethylene side arm, the silver ion system showed peak extractability at a specific length of the donating side arm; this can be explained as resulting from the best size fitted to the crown cavity (*8*).

By contrast to the 16C5 system, the corresponding 19C6 lariats with potential donor side arms at an appropriate position did not show any enhancement in extractability for most cations, due probably to its flexible framework (*8*).

Inoue et al. continued their research work by synthesizing a great number of 14, 15, and/or 16 substituted 16C5, and evaluating the change in cation binding abilities (*65, 66*). Some of the most significant results they obtained are listed in Table 3.2.1.2. It is obvious from an analysis of the table that the extractability shown by the crown ethers tested is drastically affected by position, number, type, and stereochemistry of the substituent(s) (*66*). For a better comprehension of the results, it must be kept in mind that as the metal ion in this system is extracted into the organic phase in the form of a contact ion-pair complex accompanying lipophilic picrate anion(s), access of the counteranion to the complexed cation is an important factor in determining complex stability and/or extractability (*66*). While the decrease in extractability for ligand 2) may be attributed to a larger bond angle of C14-C15-C16 atoms caused by the oxirane ring, resulting in an enlargement of the cavity size, the introduction of the methylene group in ligand 3) causes a reduction of the upward steric hindrance, and thus the approach of the counteranion is easier. Therefore, besides enlargement of the cavity, the lack of axial substitution for ligand 3) enhances extractabilities (*66*).

For ligands 4) and 5), where two substituents are fixed in the axial positions, the extractabilities increase markedly for all the examined cations. The axial bridge prohibits a flip-flop motion, and thus it seems to fix

TABLE 3.2.1.2
Solvent Extraction of Aqueous Metal Picrates with 16C5 Derivatives (dichloromethane, 25°C)

Crown – ether	% extractability					
	Na^+	K^+	Ag^+	Tl^+	Sr^+	Ba^{2+}
1) 	13.5	3.0	35.7	18.1	5.7	15.4
2) 	3.2	1.0	9.9	9.3	0.9	4.4
3) 	4.7	1.5	21.1	13.5	2.6	8.1
4) 	13.1	7.6	55.3	34.6	2.0	14.2
5) 	41.0	14.5	65.0	45.0	9.0	28.0

the two adjacent oxygens for the framework in the appropriate position for complexation (*66*).

In addition to the solvent extraction studies, there have been some reports on the stability constants of the complexes formed between this type of ligand and silver ions (*67–69*). Diester derivatives of crown ethers, extensively investigated by Izatt and coworkers (*67, 68*), may cannot be used in solvent extraction processes because they are easily hydrolyzed by contact with acidic aqueous solutions.

Izatt et al. studied the effect of combining two ligands, DC18C6 and bis-(2-ethylhexyl)-phosphoric acid (D_2EHPA), on the extraction of some metals (*70, 71*). There is a synergistic effect on the extraction of Pb^{2+} and Ag^+ as nitrate salts for a toluene solution of the two extractants, which is much more evident for the former cation. The extraction of silver increases regularly until the concentration of DC18C6 reaches the constant concentration of D_2EHPA in the tolune solution (*70*), beyond that value the distribution coefficient of the metal ion remains constant. The interpretation of both phenomena includes considerations about the stability constants of the complexes with the ligands in aqueous solution as well as the facility of solvation/desolvation of the cations and related complexes (*70, 71*).

Inoue and coworkers reported the existence of dicationic complexes in a dichloromethane phase containing some crown ethers resulting from a solvent extraction procedure directed toward alkaline metals, silver, and thallium (*72*). For silver, they found a complex of this nature with DB18C6; the easy formation of dicationic complexes is attributed to effective charge-shielding coordination by the bulky, lipophilic picrate anions in the contact ion-pair extracted complex (*72*).

Later, the same authors reported the existence of 2:2 cation–crown ether complexes using 12C4 in solvent extraction conditions similar to those reported above (*73*). Thus, the complex stoichiometry in solvent extraction is not a simple function of the size-fit concept, but it is significantly influenced by the lipophilicity of the ion-pair complex to be extracted (*73*).

Weber et al. (*74*) introduced new types of crown compounds featuring an assembly of two or three individual macrorings with different sizes and rigidities and having characteristic aromatic junctions (Fig. 3.2.1.2). They studied the cation binding and extraction abilities of the crowns toward different metal ions and concluded that several factors such as the symmetry of the crown ether, the size-fit relationship, the multiplicity, and the cooperative effects of neighboring binding sites are determinants in the interpretation of the results obtained. The efficiencies of silver extraction with this type of compound were reduced (*74*).

In conclusion, some studies have been made regarding the extraction properties of this type of ligand toward various metal ions, mainly the alkaline and alkaline-earth groups. The theoretical aspects of the equilibria involved have been investigated, especially for picrate aqueous media; the opposite situation is true for the open-chain ligands. Nevertheless, for the particular case of silver, the conventional crown ethers are not the most

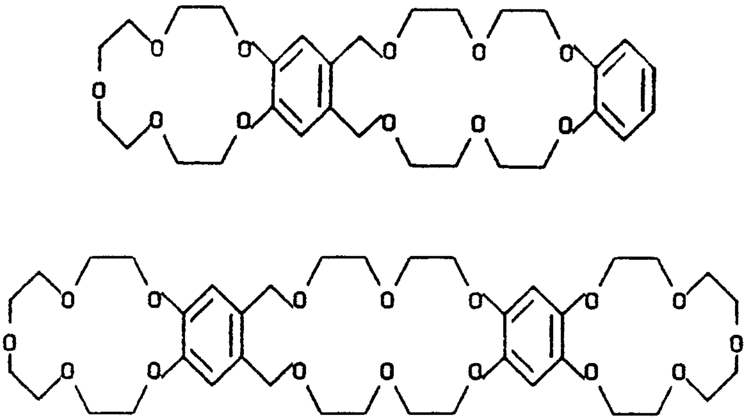


FIG. 3.2.1.2. Some ligands synthesized and tested as solvent extraction reagents for various metal ions (dichloromethane, metal picrates, 25°C).

convenient ligands because they are not efficient and, most important of all, they are not selective toward silver.

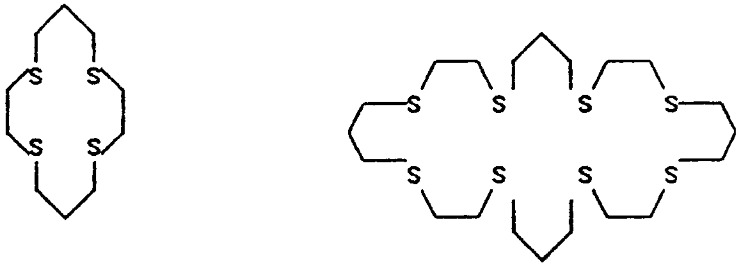
3.2.2. *With Sulfur Atoms*

Macrocycles containing sulfur atoms show a better affinity toward "soft" acids than do those containing oxygen (*59*). Thus, solvent extraction of silver by this type of ligand has been seriously studied as a result of the knowledge of an easy complexation process involving the two species in one phase.

The incapacity of the ligands to complex the alkaline and alkaline-earth metals has also increased interest in the study of the properties exhibited by this specific type of ligand.

Sevdic and Meider (*75*) extracted silver and mercury ions from chloride and perchlorate media in a nitrobenzene phase containing the extractants presented in Fig. 3.2.2.1. Both macrocycles are efficient extractants of silver for the experimental conditions used. When the concentration of chloride anion in the aqueous phase increases, the extraction efficiency decreases (*75*).

Another investigation performed by the same authors employed analogous extractants but different experimental conditions (picrate medium, 24 + 1°C, TT14C4 and HT18C6 in nitrobenzene, Figs. 3.2.2.1 and 3.2.2.2) showed that both ligands are efficient extractants of silver (*76*). The authors concluded that, as the number of sulfur atoms increases, extraction also increases, suggesting that there is a connection between the stability of the



TT14C4

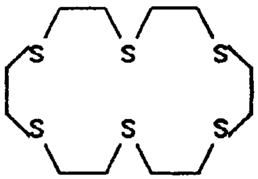
OT28C8

FIG. 3.2.2.1. Sulfur macrocyclic extractants of silver (24°C).

complexes formed and the diameter of the ring hole (*76*). As in the previous work, a detailed study on the equilibria, composition, and characterization of the complexes involved was carried out (*75*, *76*).

Sekido and coworkers (*77*) studied the extraction properties of the sulfur macrocycle TT14C4 (Fig. 3.2.2.1) for 14 different metal ions. They always used the same experimental conditions (picrate medium, macrocycle in 1,2-dichloroethane), and they concluded that only Ag^+, Hg^{2+}, and Cu^+ were effectively extracted (99.9, 89.1, and 99.4%, respectively). The extraction behavior of Cu^+ with TT14C4 was studied in detail (*77*) while using different counteranions and various solvents. Interestingly, the extraction of Cu^+ with TT14C4 and picrate into the following solvents decreased in the order nitrobenzene > 1,2-dichloroethane > chloroform > carbon tetrachloride, accompanying the decrease of the respective dielectric constants (*77*).

The same ligand was also tested by Oue and coworkers (picrate medium, macrocycle in chloroform) and they found a silver(I) extraction of 52.7%



HT18C6

FIG. 3.2.2.2. Sulfur macrocycle used in solvent extraction studies.

together with a 10% extraction of zinc(II), a 33.3% extraction of mercury(II), and a 27.3% extraction of palladium(II) (*78*).

Sekido et al. (*79*), using the same experimental conditions as in Reference *77*, tested the extraction behavior of HT18C6 and TT14C4 toward 12 different metal ions, and they concluded that only Cu^{2+} (4%), Cu^{+} (100%), Ag^{+} (100%), and Pd^{2+} (11%) were extracted. The silver complexes isolated with both ligands show a stoichiometry of cation/macrocycle/picrate of 1:1:1 for HT18C6 and 2:1:2 and 1:1:1 for TT14C4 (*79*).

The sulfur macrocycles presented in Fig. 3.2.2.3 have a strong synergistic effect on the extraction of Cu^{2+} and Ag^{+} from a sulfuric acid medium with the cation exchanger didodecyl-naphthalene sulfonic acid in toluene (*80*). Over a range of sulfuric acid concentrations, the selectivity was in the order Ag^{+} > Cu^{2+} > Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, where synergism occurs for silver and copper only (*80*). The exact nature of the organic phase species after extraction is not well known; however, Cu^{2+} and Ag^{+} are apparently extracted by the synergistic systems as mononuclear species at low metal concentrations. In view of the promising results, the authors

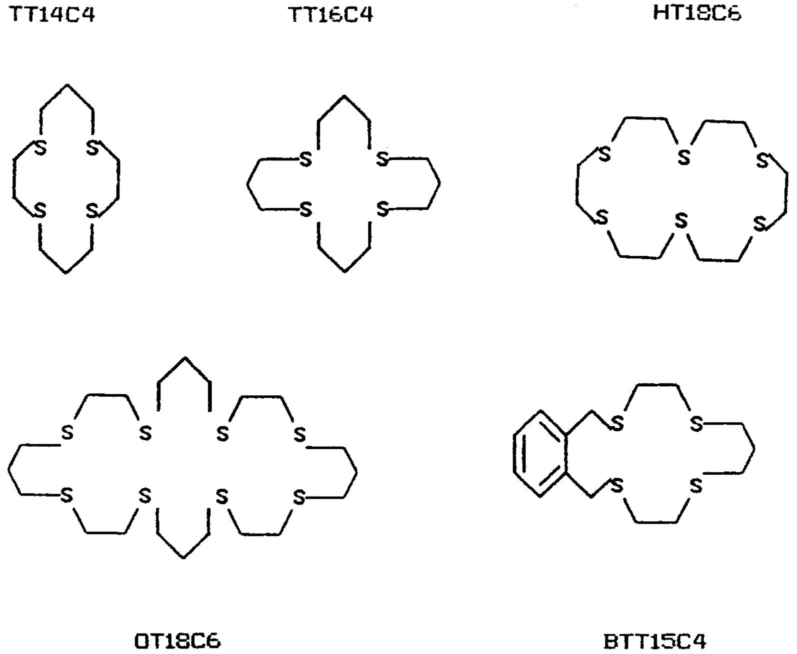
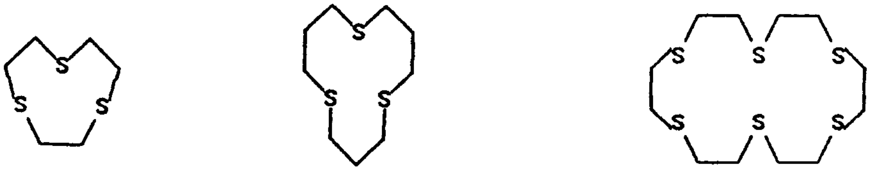


FIG. 3.2.2.3. Sulfur macrocycles used for the synergistic extraction of Cu^{2+} and Ag^{+}.



9S3 12S3 18S6

FIG. 3.2.2.4. Crown thioethers whose coordination properties toward silver were studied.

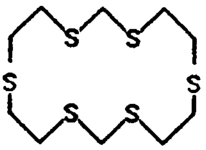
suggested that efforts should be made for a better understanding of the stoichiometry, equilibrium relationships, and structure of the species involved (*80*).

The macrocycle BTT15C4 (Fig. 3.2.2.3) in 1,2-dichloroethane was tested by Takagi and coworkers (*14*) for the extraction of copper(I) and silver. They found an extraction of 99% Cu^+ and 100% Ag^+ from an acetate/perchlorate medium.

There are very recent studies regarding the complexation and coordination chemistry of some macrocyclic sulfur ligands and silver. Blower et al. (*81*) made a contribution to a better comprehension of the coordination chemistry of the three crown thioethers presented in Fig. 3.2.2.4 toward silver. A six coordination for the complex $[Ag(9S3)_2](CF_3SO_3)$ using the conformationally favorable 9S3 crown thioether seems unusual (*81*). For this case there is a marked influence of the ligand conformation on the structure and solution chemistry of their complexes, which uniquely suits it for chelation.

There was an extensive review in 1990 regarding crown thioether chemistry (*82*). It reports several data concerning the syntheses of the complexes, as well as the analysis of the coordination properties of the different ligands toward various metal ions including silver. The coordination six of silver toward two 9S3 ligands is once more referred to; the reaction of silver perchlorate with less than two equivalents of 9S3 affords a complex that crystallizes as the cyclic trimer $[Ag_3(9S3)_3]^{3+}$ with an idealized tetrahedral [3 + 1] coordination about each Ag^+ (*82*), different from the one presented by the [AgCl9S3] complex which is substantially trigonal.

Unusual coordination numbers for the complexation of this type of ligand with silver were reported by Groot and Loeb (*83*). In fact, although the most common coordination numbers for silver are two and four, six coordination has been achieved for $[Ag(18S6)]^+$ and five coordination for the dimeric complex $[Ag_2(2,5,7,10\text{-tetrathia}[12](2,5\text{-thiophene})_2]^{2+}$. The authors studied the coordination properties of the 16S6 ligand in detail



16S6

FIG. 3.2.2.5. A thiacrown ligand for silver.

(Fig. 3.2.2.5). They concluded that in the complex [Ag(16S6)][ClO_4] the thioether macrocycle acts as a tetradentate ligand, with its coordination sphere having a distorted tetrahedral geometry (*83*).

Some substituted sulfur macrocycles with chains containing particular functional groups which can act as counteranions were synthesized (*84*, *85*). In fact, some thiacrown compounds in which benzo-azo groups were introduced as the chromogenic group (Fig. 3.2.2.6) were tested as extractants for silver and copper(II) from a hydroxide/borate/sulfate solution. The complexation process with silver ion exhibited by these two ligands was analyzed by the changes in their absorption spectra. For the first ligand, the compiled data show that silver ion uniquely bonds to the sulfur atoms in the thioether ring. On the other hand, some interaction between the metal and the *o*-hydroxylphenylazo group of the second ligand seems to occur (*84*). The selectivity of extraction showed by the second ligand toward silver was remarkable; therefore, for a pH of 10, only Cu^{2+} and Cu^+ between eight metal ions were extracted. The extraction efficiency of this ligand decreased when the pH was lowered (*84*).

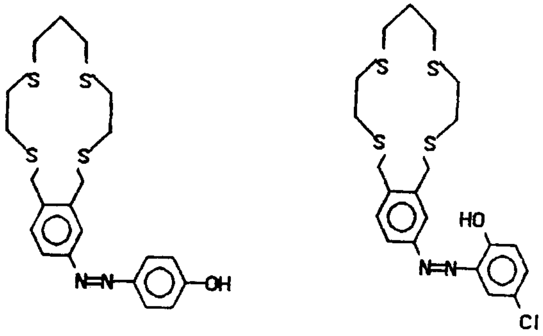


FIG. 3.2.2.6. Cyclic sulfur extractants for Ag^+ and Cu^+.

A more recent study performed by the same authors showed that the three thiacrowns presented in Fig. 3.2.2.7 are good extractants for silver and copper(I) from an acetate/sulfate medium, pH 8–9 (*85*). The authors concluded that the orthocyclophane-type reagent is adequate for the extraction and spectrophotometric measurement of Cu^+, while the metacyclophane-type reagent is more suitable for silver. The complexation sites for silver ion with this particular type of ligand are not well understood (*85*).

The extraction behavior of the two cyclic tetrathioethers TT14C4 and BTT15C4 (Fig. 3.2.2.3) were examined by Chayama and Sekido (*19*). According to the authors, the extractability of silver ion from a picrate/acetate/sulfate solution decreased in the order BTT15C4 > TT14C4. A silver ion is too large to fit the cavity of these ligands, and therefore the results obtained by x-ray crystallography and extraction study suggest that

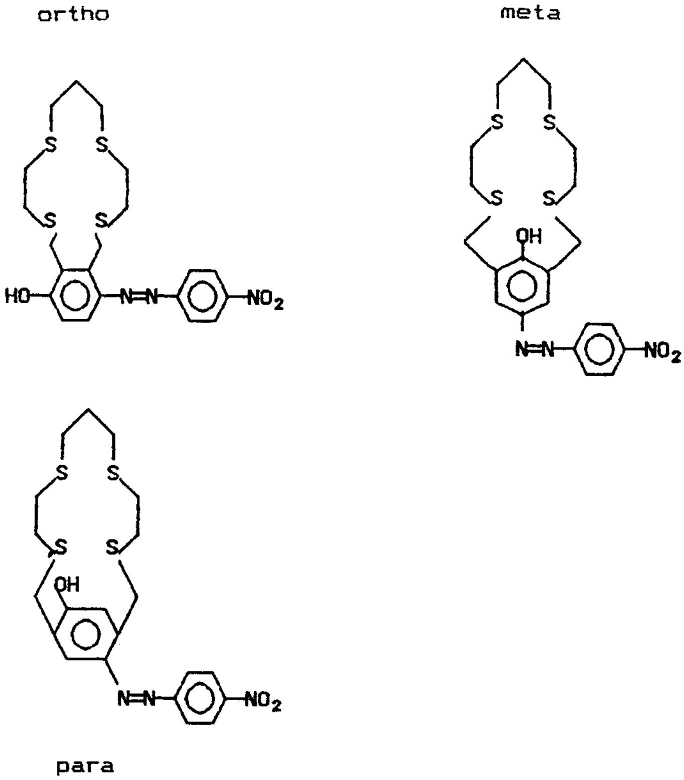


FIG. 3.2.2.7. Cyclic sulfur extractants for Ag^+ and Cu^+.

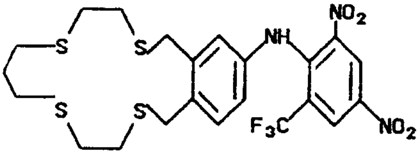


FIG. 3.2.2.8. Ligand used for the extraction of "soft" metal ions.

for TT14C4, when its concentration is lower than that of silver, the complex $[Ag_2(TT14C4)_2]Pic_2$ is extracted. With an increase in ligand concentration, the extracted complexes are the dimeric 2:2 and the 1:2 complexes, the latter being the one extracted when a large excess of ligand is used. For BTT15C4, the complex $[Ag_2(BTT15C4)_2]Pic_2$ seems to be the one extracted (*19*).

Sekido and Chayama (*86*) found that the reagent presented in Fig. 3.2.2.8 is a good ligand for the extraction and spectrophotometric determination of univalent "soft" metals like Ag^+ and Cu^+. In fact, Ag^+ is completely extracted by this ligand into 1,2-dichloroethane from aqueous solutions with a pH above 8. Cations such as Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Fe^{3+}, when present in a two hundredfold amount relative to Ag^+, do not interfere with the extraction and spectrophotometric determination of silver (*86*).

For specific sets of experimental conditions, sulfur macrocycles are, in general, good and selective extractants for silver, mercury, and copper(I). Thus, these results are perhaps the reason why there have been several extraction studies made with these types of ligands. However, it must not be forgotten that their syntheses are not easy, they are expensive, and that using only them in an industrial application for the recovery of noble metals would not be economically feasible.

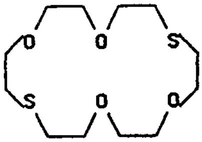
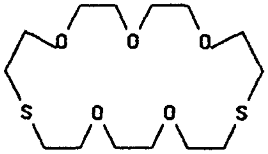
3.2.3. *With Oxygen and Sulfur Atoms*

As a result of the available data for the complexation/extraction of silver by crown ethers and sulfur macrocycles, the same type of studies using crown ethers with sulfur atoms has increased.

Buschmann (*87*) studied the complexation properties of this type of ligands with the silver ion in methanol at 25°C (Table 3.2.3.1).

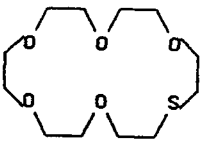
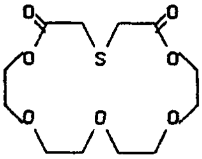
Table 3.2.3.2 presents some data concerning complexation studies done by Izatt and coworkers (*67, 68*). As expected, it can be seen that the silver complex is the most stable within those studied. The second ligand of this table is not suitable for a solvent extraction study because of its instability in acidic medium. Furthermore, its affinity for silver is lower than that of the corresponding nonester ligand (*68*).

TABLE 3.2.3.1
Stability Constants for 1:1 Complexes with Ag^+ in Perchlorate Medium

Ligands	log K $(cm^3 mol^{-1})$
	9.85
	10.33

Lee and coworkers (*88*) measured the equivalent conductance of some univalent cation perchlorates in methanol containing 1,10-dithia-18-crown-6 (DT18C6). The selectivity order showed by the ligand was $Ag^+ > Tl^+ > NH_4^+ > K^+$. The great stability observed for the silver complex was attributed to the favorable exothermic heat of reaction between the polarizable "soft" cation and the "soft" sulfur centers (*88*).

TABLE 3.2.3.2
Stability Constants of the 1:1 Complexes (methanol, 25°C)

Ligands	Ion	log K
	Ag^+ Ba^{2+} Na^+ K^+	> 5.5 3.4 + 0.1 2.57 + 0.02 3.61 + 0.02
	Ag^+	3.05 + 0.05

Igarashi and Suzuki (*89*) analyzed the degrees of complex formation exhibited by six different polyoxathia rings, and they concluded that complexing efficiencies increase with an increasing number of sulfur atoms. They also studied the stoichiometry of a ring with two sulfur atoms with silver dichromate, and they found a Ag^+/ligand proportionality of about 3:1 (*89*).

Tor and coworkers (*90*) synthesized and studied some macrocyclic thiolactones and tested their binding properties by IR spectrometry. IR spectroscopy of mixtures of each of the dimeric macrocycles whose general structure is presented in Fig. 3.2.3.1 (n = 4–7) with each of the metal salts $Pb(NO_3)_2$, $HgCl_2$, and $AgNO_3$ in Nujol mulls indicated no binding of Pb^{2+} and Hg^{2+}, but there was binding of $AgNO_3$ to the even numbers of the dithiolactones (n = 4, 6). In addition, analysis of the spectra obtained showed that the sulfur atoms of the thiolactone groups appear to act as binding sites in these complexes (*90*). The authors pointed out that the presence of carbonyl groups, as tools for reducing the conformational mobility which is typical for the majority of the macrocyclic thioethers, may enhance the binding selectivities of this type of ligands. Nevertheless, as reagents for solvent extraction from acidic solutions, lactones are not a good option, as mentioned before.

The extraction properties of dibenzo-1,10-dithia-18-crown-6 were studied by Gloe and coworkers (*91*). The results obtained show that the extraction of Ag^+, Pd^{2+}, and Au^{3+} is much greater than that of Hg^{2+} and Cu^+, the coordination of the metal ions with the sulfur atoms being decisive for the extraction. While the variation of the substituents on the macrocyclic ring from methyl to chloromethyl groups influenced the extraction power considerably, substitution on the benzo groups showed a less strong effect (*91*). The influence of the diluent and counteranions on extraction were also studied. A synergistic extraction for silver was found when mixtures

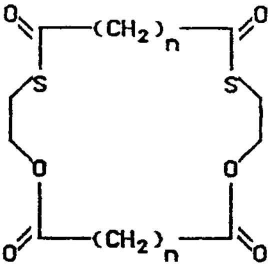
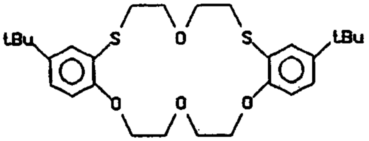
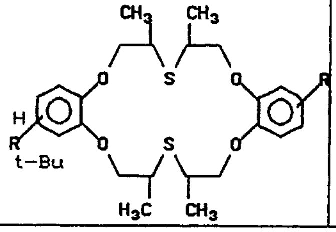


FIG. 3.2.3.1. General structure of some thiolactones.

TABLE 3.2.3.3
Stability Constants (1,4-dioxane/water, 75% v/v, 25°C) of the Complexes Ligand-Ag^+ and Extraction Constants (nitrate medium, water/benzene)

Ligands	log K_1	log K_2	log K_{ex1}	log K_{ex2}
	5.6	2.5	–	–
 R = H	–	–	1.6	2.8
R = t-Bu	–	–	2.6	4.6

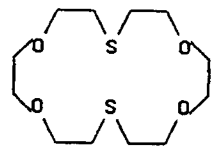
of bis-(2-ethylhexyl)-phosphoric acid (D_2EHPA), caprylic acid, or tributylphopshate (TBP) were used (*91*).

A specific ligand of this type, the 8,9;17,18-bis(4′-*tert*-butylbenzo)-1,7-dithia-18-crown-6, was also tested as an extractant for silver (*92*). From metal nitrate/picric acid aqueous solutions to chloroform solutions of the ligand, it was shown that Ag^+, Hg^{2+}, and Pd^{2+} were extracted more efficiently than K^+, Rb^+, and Sr^{2+}, as would be expected (*92*).

Dietze and coworkers measured some stability and extraction constants of silver ion with a few macrocycles of this type, Table 3.2.3.3 (*19*). The extraction and complex formation investigations presented in this work demonstrate the absence of a macrocyclic effect on extraction, showing clearly that similar open-chain compounds exhibit higher distribution ratios (*19*), see Table 3.1.5.2. The influence of structural factors on extraction is remarkable; thus, when the spatial rearrangement of sulfur atoms in the molecule is more favorable for silver coordination, as it is the case for the last ligand of Table 3.2.3.3, the extraction increases markedly (*19*).

The distribution coefficients for $AgNO_3$, $Pb(NO_3)_2$, and $Cd(NO_3)_2$ for the water–toluene system, as well as the values of log K (H_2O) for the interacting metals and DT18C6 (*71*), are presented in Table 3.2.3.4. For this set of experimental conditions, the efficiency for the extraction of silver is low, although it is better than for the other two cations tested (*71*).

TABLE 3.2.3.4
Values of *D* and log *K* ⟨H_2O⟩ for the Extraction of the Ions Presented with DT18C6 ($[M^{n+}] = 10^{-4}$ M; [DT18C6] $= 10^{-1}$ M)

Ion	D	log K	Macrocycle
Ag^+	0.15	4.34	
Pb^{2+}	0.06 + 0.06	3.13	
Cd^{2+}	0.09 + 0.03	–	

Syntheses of this type of ligand containing one molecule of ferrocene were also done (*93*) (see Fig. 3.2.3.2). The ligands showed good extraction/selectivity for Hg^{2+} and Cu^{2+}. They are also good extractants for Ag^+, but the complexes formed decompose quickly (*93*). The decomposition process is the result of oxidation of the iron atom of the ferrocene molecule, caused by the incorporated silver ion. Such a process did not happen for the other metal ions tested (*93*).

The ligand shown in Fig. 3.2.3.3 was also tested as an extractant for several metal ions (*74*). The extractability of the silver ion (picrate medium, ligand in 1,2-dichloromethane, 25°C) was the highest among alkaline, alkaline-earth, and thallium, as would be expected from the presence of a binding site with four "soft" sulfur donor atoms (*74*).

FIG. 3.2.3.2. Macrocycles containing one molecule of ferrocene.

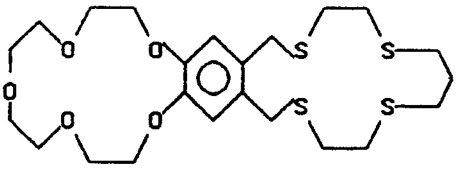


FIG. 3.2.3.3. Two individual macrorings joined into one by an aromatic junction.

Interesting work involving this type of ligands contained in polymeric structures was carried out by Oue and coworkers (*78, 94, 95*). These authors showed that there is greater efficiency of the polymeric derivatives in relation to the monomeric analogues on the extraction level. The ligands presented in Fig. 3.2.3.4 were synthesized (*94*), and the researchers tested their extractability and selectivity properties toward eight cations (Table 3.2.3.5) (*78, 95*).

By analyzing the above data it can be seen that the monomeric ligands exhibit better selectivity toward the silver ion than do the other ligands; nevertheless, the extraction efficiencies of the bis and poly derivatives are better than those obtained using the monomeric analogues, although their selectivity decreases markedly, mainly in the presence of the mercuric ion.

An attempt was made to study the complex formation between silver nitrate and the mono- and bis-(thiacrown-ethers) by conductometric analysis (*95*). Plots of the molar conductivities against the concentration ratios of the thiacrown unit/Ag^+ revealed the formation of 1:1 complexes with the mono derivatives. Although the discontinuous conductivity change is not yet understood for the (bis derivatives)/(Ag^+ system) (*95*), the break at $L/M = 2$ suggests the formation of 2:1 complexes, at least for conditions involving an excess of ligand.

Silver extraction using binary and quaternary systems of cations was also studied (*78*). The results showed that for ligands P1, P2, and B2 (Fig. 3.2.3.4) in the presence of both mercury and silver, only the former is extracted due to the formation of a mercuric insoluble complex. All other extractions from binary and quaternary mixtures were selective for silver, even in the presence of other heavy or transition metal ions (*78*).

In conclusion, it can be said that these ligands are good extractants of silver and extract Ag^+, Hg^{2+}, and Cu^+ selectively. However, research verifying these properties for a hydrochloric acid/chloride aqueous media are nonexistent. A disadvantage inherent to this type of ligand, as well as to all macrocyclic ligands, is their complicated syntheses and high cost. Thus, there is little interest in them for industrial application.

3.2.4. With Nitrogen Atoms

As for the analogous open-chain amines, the extraction properties of the ligand 1,4,7,10,13,16-hexa-aza-octadecane (hexacyclen, Fig. 3.2.4.1) toward different metal ions, including silver, have been studied (*96*).

The solubility of the ligand in water is real; thus, Bontchev and coworkers (*96*) mixed aqueous solutions of sodium perchlorate, picric acid, or dodecylbenzene sulfonate, the metal in study, a buffer, and the hexacyclen ligand. After 30 minutes of interaction (with some heating, depending on the metals), methyl isobutyl ketone was added to make the extraction. The

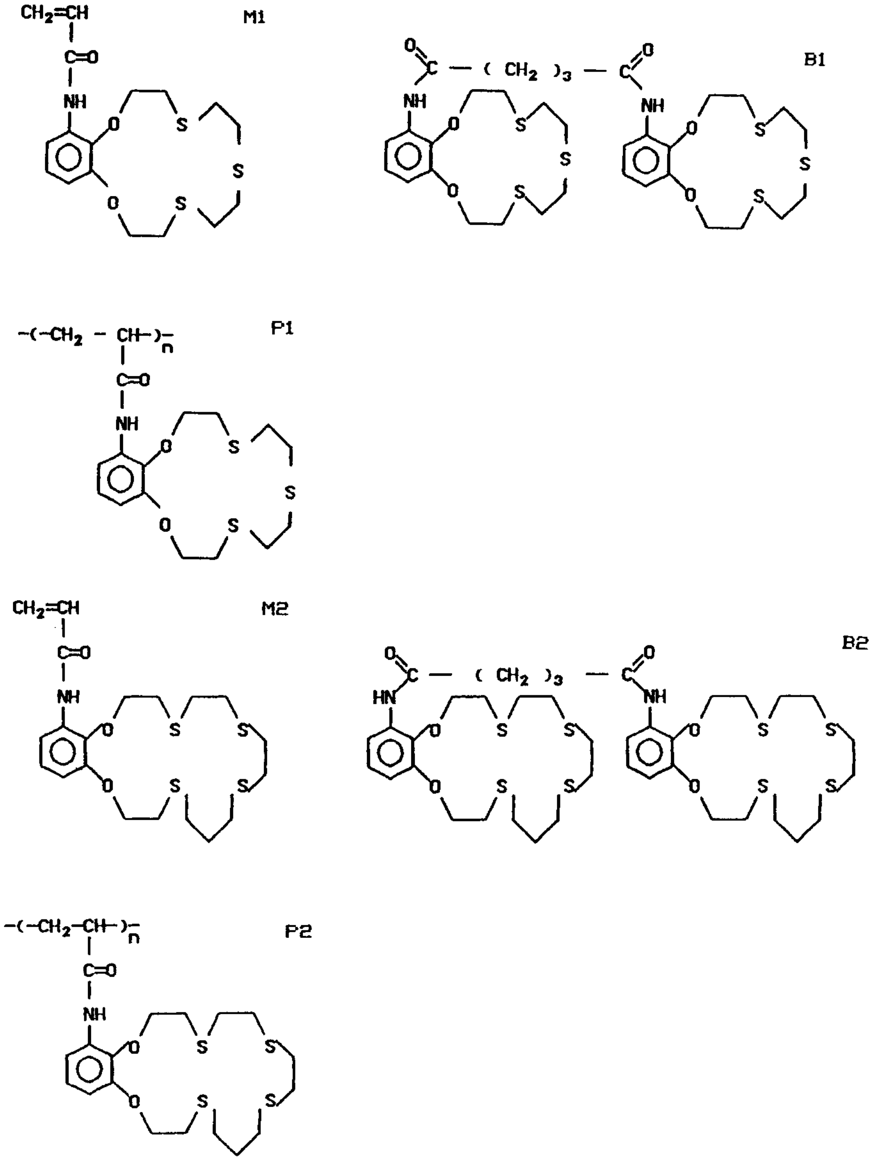


FIG. 3.2.3.4. Mono-, bis-, and poly(thiacrown-ether) derivatives.

TABLE 3.2.3.5
Extraction Properties of the Ligands Indicated toward Several Ions (25°C, water/chloroform, picrate medium)

Ligands	% of extraction							
	Na^+	K^+	Fe^{3+}	Cu^{2+}	Ag^+	Zn^{2+}	Hg^{2+}	Pb^{2+}
M1	0.4	0.2	0.1	0.0	70.3	0.4	0.0	0.9
M2	0.6	0.3	0.1	0.2	71.6	0.4	0.0	1.3
B1	0.3	0.1	0.3	0.6	86.7	1.3	25.1	1.5
B2	0.4	0.2	0.3	0.7	88.4	1.5	25.3	1.5
P1	0.6	0.4	0.4	0.8	90.6	1.4	90.4	1.5
P2	1.0	0.3	0.3	1.5	90.6	2.1	90.4	1.5

results obtained showed that such ions as Ag^+, Hg^{2+}, Cu^{2+}, Pt^{2+}, and Pd^{2+} can be quantitatively extracted (*96*). The flexibility of the macrocycle and the good donor capacities of the nitrogen atom seem to result in the formation of complexes with quite a different structure for each metal. In terms of selectivity, an effective separation from Fe^{3+} is made for Pt^{2+} and Pd^{2+} and $Fe^{3+}/M^{n+} = 10^4$, for Hg^{2+} at 10^3, for Cu^{2+} at 10^2, and for Ag^+ at 5 (*96*). Nothing has been said regarding the mechanisms of extraction and/or complexation.

Interesting work performed by Suet and coworkers (*97*) analyzed the nature of the silver(I) complexes of four different macrocyclic tetramines (Fig. 3.2.4.2). When added to an aqueous solution of silver perchlorate or nitrate, ligands 1) and 2) form a silver mirror on the walls of the beaker together with an orange solution typical of the silver(II) salts (*97*). The same phenomena does not take place with ligands 3) and 4), although a white precipitate appears when ligand 3) is used. A careful study of the experimental results shows that Ag^+ suffers a dismutation process by ligands 1) and 2) (Fig. 3.2.4.2) and forms Ag^{2+} complexes, whereas with ligands 3) and 4) there are normal complexation phenomena. An expla-

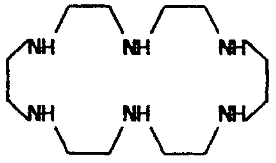


FIG. 3.2.4.1. Structure of hexacyclen.

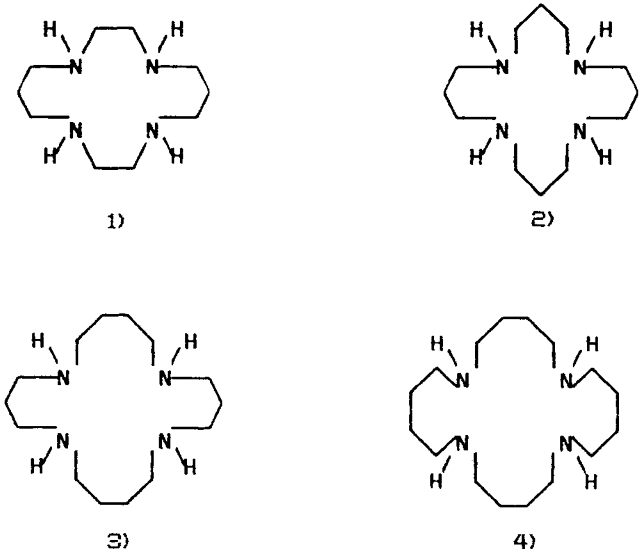


FIG. 3.2.4.2. Macrocyclic ligands studied for the complexation of silver ion.

nation of the dismutation process seems to be the best fit of the Ag^{2+} ion to the cavity of the macrocycles as well as the preference of the latter ion to assume a more favorable coordination structure (*97*).

A potentiometric study carried out to clarify the complexation characteristics presented by ligands 3) and 4) toward silver was also performed. The stability constants found for the complexes are presented in Table 3.2.4.1 (*97*). For the 2:1 complexes, the values obtained are very similar to those measured for aliphatic monoamines. Thus, it seems logical to consider that only one nitrogen establishes complexation with Ag^+ by the ligand (*97*).

TABLE 3.2.4.1

Stability Constants of the Complexes L/Ag^+ (aqueous nitrate medium, 20°C)

Ligand	Stability constants in solution		
	log K (1:1)	log K (3:2)	log K (2:1)
3)	$pK_s = 8$	16.6	8.0
4)	5.7	–	8.3

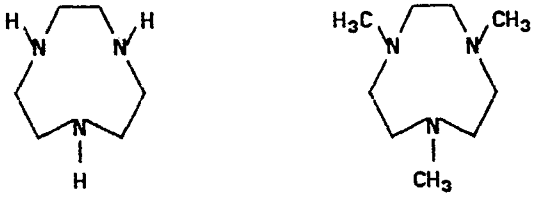


FIG. 3.2.4.3. Ligands studied for the complexation of silver and mercury (acetonitrile, PF_6^-, 25°C).

Stockheim and coworkers (*98*) reported the synthesis and some crystal structures of complexes of the two ligands shown in Fig. 3.2.4.3 with Ag^+ and Hg^{2+}. The authors found 1:1 complexes for both ligands with Ag^+, as well as 2:1 complexes when an excess of ligand was used. Binuclear species were obtained when equimolar amounts of the first ligand and the metal ion in pyridine were used (*98*).

The main disadvantage of this type of ligand for solvent extraction is its easy solubility in water, which is why there have not been many extraction studies using it. Nevertheless, the alkylation and/or acylation of N donor atoms with long chains can improve its hydrophobicity, and this can perhaps justify more extraction/complexation studies. For the particular case of silver, one can hope for a remarkable selectivity in extraction.

3.2.5. With Oxygen and Nitrogen Atoms

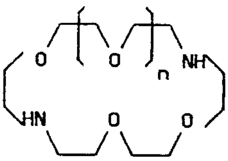
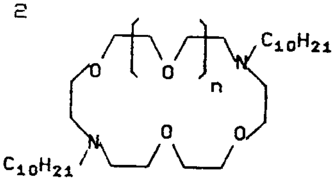
There are some data in the literature concerning the complexation of various azacrown ethers with silver, but the inverse situation is true for extraction studies.

The synthesis of the complex in Fig. 3.2.5.1 was reported (*99*). This complex, which exhibits an amphiphilic nature, displays surface activity and is readily capable of micelle formation. The complexation process was carried out by mixing equimolar amounts of silver nitrate and the organic ligand in aqueous solution (*99*).

Buschmann (*7*, *87*) measured the stability constants of different ligands of this type with silver (Table 3.2.5.1). The author verified that there is not an increase in complex stability with all the ligands compared to noncyclic nitrogen-containing ligands (*7*).

Spiess et al. (*100*) measured the stability constants of silver complexes with some unsubstituted diaza macrocycles in two aprotic solvents, dimethylsulfoxide and propylene carbonate. The authors found complexes with a 1:1 stoichiometry only, and they also verified that silver complexes with the ligands studied were less stable in DMSO and more stable in PC than in water and methanol (*100*).

TABLE 3.2.5.1
Stability Constants of the Complexes of the Indicated Ligands with Silver (25°C, methanol, perchlorate medium)

Ligands	log K (M^{-1})
	
n = 0	7.63
n = 1	10.02
n = 2	9.60
	
n = 2	10.28

The same kinds of studies were carried out by Cox and coworkers who measured the variation of the stability constants of the complexes formed with different proportions of water and acetonitrile (*50*). For a constant ionic strength of 0.1 M in tetraethylammonium perchlorate, they found the stability constants listed in Table 3.2.5.2.

The preferential solvation of silver ion by acetonitrile in the mixtures results in a sharp decrease in the stability constants as acetonitrile is added to water, but the effect is partially compensated for by a corresponding

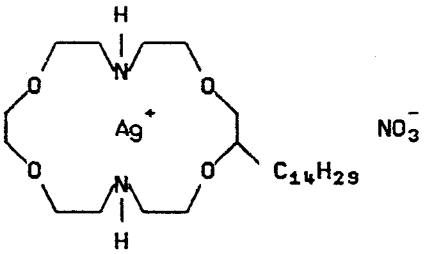
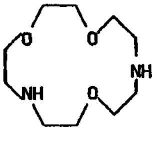
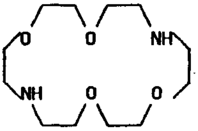


FIG. 3.2.5.1. A complex of a diaza macrocycle with silver.

TABLE 3.2.5.2
Stability Constants of the Silver Complexes Involving the Indicated Ligands (25°C, I = Et_4NClO_4, 0.1 M)

Ligands	log K		
	Water	1:1 mixt.	Acetonitrile
	5.88	4.53	6.11
	7.70	6.22	7.76

decrease in the free energies of the complexes (*50*). The stability constants of the complexes formed by the second ligand of Table 3.2.5.2 with silver, as well as with some other metal ions, were measured in various solvents at 25°C (*101*). In most cases the stability constants decrease in the order $Ag^+ > Tl^+ > Li^+ > Na^+ > Cs^+$, and this is an indication that in solvents which are good donors (e.g., DMSO) complexes of Li^+ are less stable than those of the other alkali metals. There is strong bonding between Ag^+ and the two nitrogen atoms of the ligand, with the exception of acetonitrile in which there is competition between the solvent and ligand for Ag^+, as referred to earlier (*101*).

Spiess and coworkers (*102*) compared the stability of silver complexes involving this type of ligand with those of cadmium and lead (Table 3.2.5.3) as calculated by potentiometry and spectrophotometry.

There are more complexation studies concerning substituted diaza macrocycles (*103–106*). Dalley and coworkers synthesized different diaza macrocycles with substituents of the hydrazine type (*103*) and measured their stability constants with some metals (Table 3.2.5.4). The log K values for the interaction of tetra-aza-18-crown-6, ligand 1), with Ag^+, Pb^{2+}, and Cd^{2+} were much lower than those for the interaction of the symmetrical triaza-18-crown-6, ligand 2), with the same cations. The authors also verified that ligand 1) reduced silver ions to silver metal when a solution of the ligand and the silver ion in DMSO was allowed to stand for several days (*103*).

TABLE 3.2.5.3
Stability Constants of the Indicated Complexes (25°C, methanol, perchlorate medium)

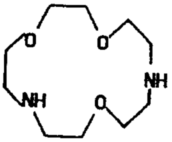
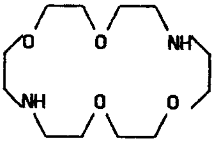
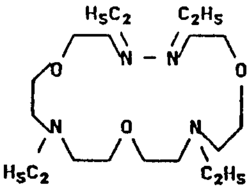
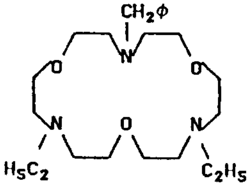
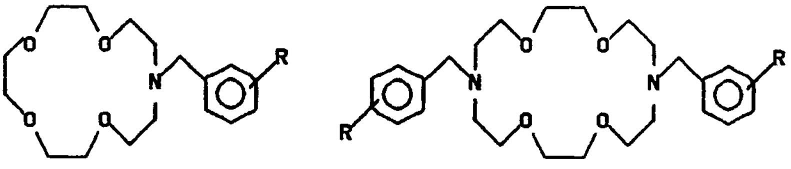
Ligands	Complexes	log K
	AgL^{+} Ag_2L^{2+} PbL^{2+} Pb_2L^{4+} CdL^{2+} Cd_2L^{4+}	7.61 ± 0.05 11.21 ± 0.10 7.87 ± 0.02 11.36 8.72 ± 0.01 11.99 ± 0.08
	AgL^{+} Ag_2L^{2+} PbL^{2+} Pb_2L^{4+} CdL^{2+} Cd_2L^{4+}	10.18 ± 0.01 13.51 ± 0.05 9.48 ± 0.01 12.30 ± 0.18 7.83 ± 0.02 11.41 ± 0.08

TABLE 3.2.5.4
Stability Constants of Complexes Involving the Indicated Ligands and Metals (25°C, DMSO, perchlorate medium)

Ligands	Cations	log K
	Ag^{+} Pb^{2+} Cd^{2+}	3.46 ± 0.05 < 0.5 < 0.5
	Pb^{2+} Cd^{2+}	4.32 2.62



Aza – 15 –Crown – 5 Diaza – 18 – Crown – 6

FIG. 3.2.5.2. Ligands used for the complexation of silver and some other metals (25°C).

The stability constants of the silver, lithium, and sodium complexes of the ligands shown in Fig. 3.2.5.2 were measured by Gokel and coworkers by potentiometric methods using acetonitrile as the solvent (*104*). Lithium and sodium binding is higher than silver binding with the aza-15-crown-5 derivative but lower with the diaza-18-crown-6 species. Thus, the authors concluded that when the nitrogen/oxygen ratio in the macroring donors is high (diaza-18-crown-6 = 0.5), Ag^+ binding is high and alkali metal cation binding is low. As the ratio decreases (aza-15-crown-5 = 0.25), Ag^+ binding decreases and alkali metal cation binding increases (*104*).

Ossowski and Schneider (*105*) synthesized some aza crown ethers with quinone side chains and studied their complexation and cation binding properties by UV/Vis spectrophotometry. The complexing ability of the ligand presented in Fig. 3.2.5.3 was studied in detail. The authors verified that silver and thallium ions are tightly held in the aza crown ring by a strong interaction with the nitrogen atom. The nitrogen lone pair points to the metal ion in the ring, and the substituent group is located externally (*105*).

Matsumoto and coworkers (*106*) verified that there is a selective attachment of the silver ion to the ligand presented in Fig. 3.2.5.4. Thus, the

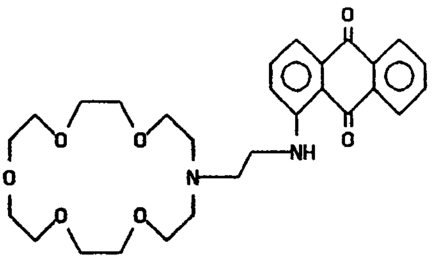


FIG. 3.2.5.3. The ligand studied for the complexation of some metals (propylene carbonate, 25°C, perchlorate medium).

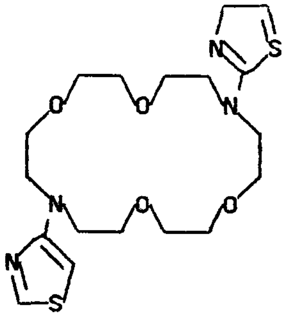


FIG. 3.2.5.4. A selective ligand for silver (25°C, DMF/D_2O, perchlorate medium).

addition of silver perchlorate to a solution of the ligand resulted in remarkable spectral ^{13}C-NMR changes due to complexation, whereas potassium perchlorate induced only slight changes. Since the signals for the 2- and 4-position carbons of the heterocyclic ring shifted significantly, side arm participation in complexation exists (*106*).

A study regarding the determination of silver ion was carried out by Morosanova and coworkers (*107*), who studied the variation of the distribution coefficients of the cation upon extraction by some diaza macrocycles. An extraction-photometric method was introduced for the silver ion, based on the selective extraction by a chloroform solution of an aza macrocycle and triphenylphosphine followed by photometric determination in the organic phase using tyrodine (*107*). The authors pointed out that the silver ion can be determined in the presence of large amounts of Pd^{2+}, Au^{3+}, and other metals (*107*).

Previous work performed by the same authors studied the extraction abilities of some diaza macrocycles toward Ag^+, Hg^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Fe^{3+}, Mn^{2+}, and Pd^{2+} (*108*) (Fig. 3.2.5.5). The unsaturated

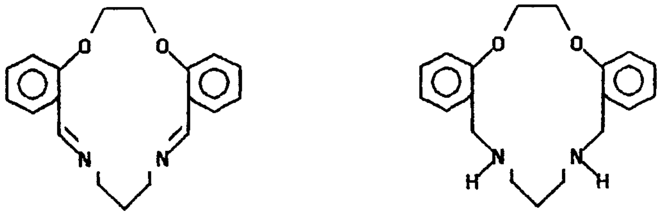


FIG. 3.2.5.5. Ligands used for the extraction of several metal ions.

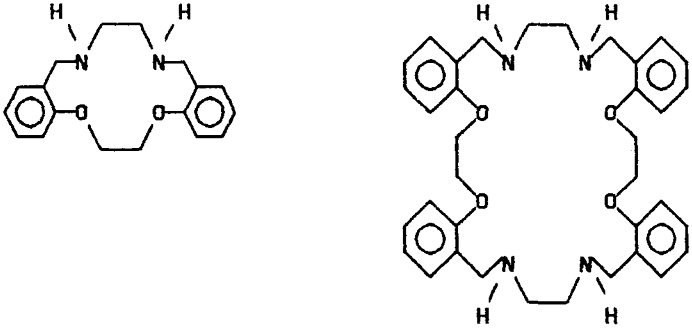


FIG. 3.2.5.6. Ligands tested as analytical extractants of several metal ions.

diaza macrocycle only extracts Ag^+, whereas the corresponding saturated one extracts Ag^+, Hg^{2+}, Cu^{2+}, and Pd^{2+}. Different counteranions and organic solvents were used in order to verify their influence on the extraction abilities (*108*).

The authors also tested the ligands presented in Fig. 3.2.5.6 as analytical extractants for transition metals (*109*). The distribution coefficients and degree of extraction of Ag^+, Hg^{2+}, Zn^{2+}, Cu^{2+}, and Co^{2+} were determined as functions of pH in the water–chloroform system, as well as the stability constant of the 1:1 Ag^+–diaza macrocycle ($\log K = 3.9$) (*109*).

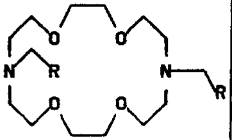
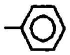
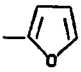
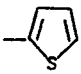
Another paper deals with the same kind of aza macrocycles as extractants for the determination of a few metal ions including silver (*110*). The method was based on the extraction of the metal by a specific diaza macrocycle in the presence of picric acid (pH 5.4) to an organic phase of 1,2-dichloroethane and the subsequent formation of colored complexes with rhodamine dyes (*110*).

A triaza analogue of dibenzo-18-crown-6 was tested as an extractant for silver (*111*); the extracted complex had the structure AgLA (A = dipicrylaminate).

A new extraction scheme for silver by a specific diaza macrocycle is based on new electric conductivity data and considerations of the extraction equilibria (*112*). The authors assumed the formation of $Ag_2L_2Pic_2$ (L = macrocycle, Pic = picrate) instead of AgLPi, as proposed previously (*112*).

Tsukube et al. (*113*) tested the extraction and selectivity properties of some ligands of the side arm type aza macrocycles, Table 3.2.5.5. The results show that the nature of the ligating side arms markedly influence the extraction efficiency and selectivity. However, although they are good extractants of silver in general, they also seem to be reasonable ligands for lead.

TABLE 3.2.5.5
Extraction Properties of the Three Indicated Ligands (25°C, water/chloroform, perchlorate medium)

Ligand	R	% of extraction			
		Na^+	K^+	Ag^+	Pb^{2+}
		1.7	3.4	85.7	11.8
		2.4	5.2	87.4	25.0
		< 1	3.2	37.8	16.4

In conclusion, these ligands are, in general, very good complexants of silver ions, and all the work reported here proves it. In terms of extraction, they are not the most suitable ones because they seem to be nonselective for the silver ion.

3.2.6. With Nitrogen and Sulfur Atoms

An important article by Reid and Schroder (*114*) aimed to summarize the coordination chemistry of mixed S- and N-donor macrocycles presented in Fig. 3.2.6.1 toward several metal ions. A particular section regarding the complexation of the silver ion by these ligands describes the crystalline structure of the complexes obtained. For the complex involving the first ligand, the silver ion may be regarded as five-coordinated to an NS_4 donor set with an additional long-range interaction of the second N-donor. For the second ligand, two types of complexes resulted: a major component with an N atom which does not interact with silver and a minor component where the 4S- and 2N-coordinate directly with the silver ion (*114*).

FIG. 3.2.6.1. Ligands used for the complexation of several metals (methanol/water, reflux).

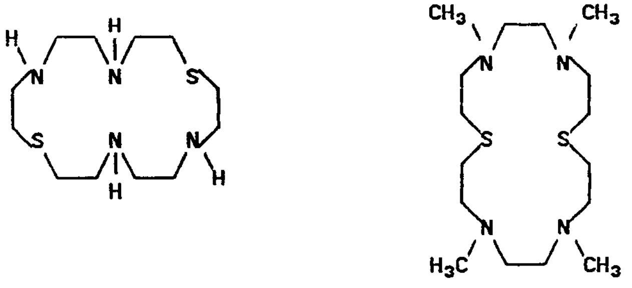


FIG. 3.2.6.2. Donor macrocycle complexants of silver ion (methanol, nitrate medium, 25°C).

The syntheses of some related donor macrocycles have also been reported (*115*) (Fig. 3.2.6.2) as well as their complexing abilities for silver ion. For a complex involving the first ligand, the silver ion is hexa-coordinated by the N_4S_2 donor atoms in a distorted octahedral geometry (*115*).

Extraction studies involving the use of open-chain and macrocyclic compounds containing nitrogen and sulfur atoms for the recovery of several metals from acidic aqueous solutions were performed (*116*). The macrocyclic ligands showed selectivity toward silver and palladium (*116*).

The extraction of calcium, silver, mercury, and palladium ions by four macrocycles with N- and S-donor groups was studied in detail by Zolotov and coworkers (*117*). Extraction constants and the composition of the extracted complexes were established for silver (*117*).

Thiaza derivatives of dibenzo-15-crown-5 were tested for the extraction of silver and mercury from picrate medium (*118*). Extraction from weakly acidic or neutral solutions resulted in 1:1:1 metal/thiaza/picrate complex formation in the organic phase, as determined by equilibrium shifts, IR, and electronic spectral studies (*118*).

For the selective extraction and determination of silver, Poddubynkh and coworkers (*119*) used the macrocycle presented in Fig. 3.2.6.3.

Knowledge of the extraction abilities of this type of ligands is limited; perhaps more studies involving it would be worthwhile.

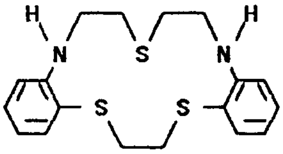


FIG. 3.2.6.3. N- and S-donor macrocycle used for the selective extraction and determination of silver (dipicrylaminate or picrate medium, pH 5–9, 1,2-dichloroethane or chloroform).

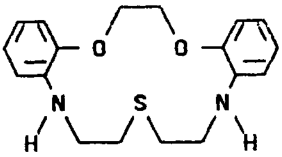


FIG. 3.3.1.1. Ligand with N-, S-, and O-donor atoms.

3.3. Miscellaneous

3.3.1. Macrocyclic Compounds

A few articles report extraction and/or complexation studies of some metals involving macrocycles containing N-, S-, and O-donor atoms (*119, 120*). Kardivarenko and coworkers (*120*) measured the electric conductivities of Hg^{2+} and Ag^{+} complexes with the ligand presented in Fig. 3.3.1.1. These determinations were carried out in dimethylsulfoxide, 1,2-dichloroethane, and nitrobenzene. Association constants and limiting molar electric conductivities were calculated for the silver complexes in picrate medium (*120*).

Rybakova and coworkers (*121*) tested the extraction properties of six macrocyclic polyethers containing phosphoryl and thiophosphoryl groups toward 19 metal ions. The metals are virtually not extracted by the ligands containing phosphoryl groups only or by the thiophosphoryl macrocycles at pH 1 to 5. Nevertheless, the latter ligands do extract Ag^{+}, Hg^{2+}, and Pd^{2+} quantitatively from relatively concentrated nitric or perchloric acid solutions (*121*).

3.3.2. Cyclic Compounds

Some authors performed extractions of metal ions by using a type of ligand which can be called “cyclic compounds.” In fact, Vanifatova et al. (*122*) used the radical-containing complexing reagent illustrated in Fig. 3.3.2.1 for the extraction of Pd^{2+} from a hydrochloric acid solution into a chloroform phase. The extraction and ESR spectra of silver complexes involving this ligand were also examined (*122*).

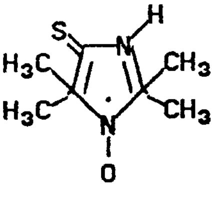


FIG. 3.3.2.1. Ligand used for the determination of Pd^{2+}, Ag^{+}, Au^{3+}, Hg^{2+}, and Pt^{2+}.

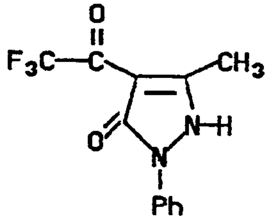


FIG. 3.3.2.2. Structure of 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone.

Less recent studies regarding silver extraction were carried out by Dzimko and coworkers (*123*) who tested 3,4,5-trisubstituted pyrazoles. Hasany and Qureshi (*124*) used 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone (Fig. 3.3.2.2) as an extractant for metal ions of Groups Ib, IIb, and IIIA to VA. Selective group and individual separations were proposed by the authors on the basis of pH control and masking effects of the counteranions (*124*).

3.4. Cryptands

The major part of the papers concerning the interaction between silver and other metals with this type of ligands are complexation studies and transport of ions through liquid membranes.

The cryptand ligands were introduced by Lehn and coworkers (*125*), who first reported the strong binding of alkaline and alkaline-earth cations to this type of compound. In addition, they also verified a remarkable cation selectivity. Since then, the development of extraction/complexation studies of Pb^{2+}, Ag^{+}, and Tl^{+} has increased.

Consequently, Spiess and coworkers (*102*) studied the nature and stability of some macrobicyclic complexes of Ag^{+}, Cd^{2+}, and Pb^{2+} involving the cryptands presented in Fig. 3.4.1. By using potentiometry and spec-

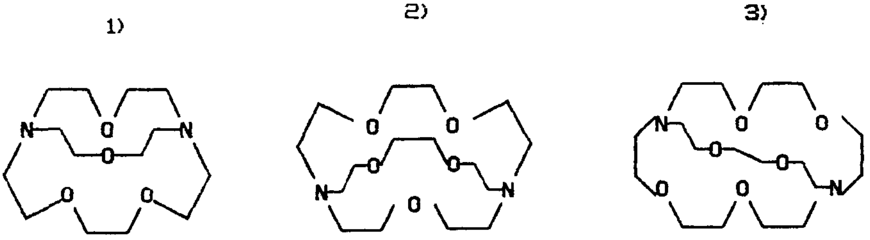


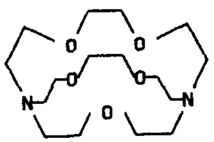
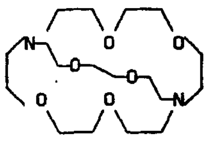
FIG. 3.4.1. Cryptands used for the complexation of silver, cadmium, and lead (anhydrous methanol, perchlorate medium, 25°C).

trophotometric methods, the authors found the formation of mononuclear complexes, ML^{n+}, as well as binuclear complexes M_2L^{2n+}, for all the cryptands tested. The former complexes exhibit a significant "cryptate effect" for Ag^+, Pb^{2+}, and Cd^{2+}, which was not verified for Cu^{2+} and Zn^{2+} (cryptate effect: complexes formed with a bicyclic ligand for a given medium are more stable than the correspondent monocyclic ligand having an analogous size cavity). The greater stability showed by ligand 2) and Ag^+, Pb^{2+}, and Cd^{2+} (Fig. 3.4.1) can be explained on the basis of the most suitable cation/cavity ratio.

The same authors presented the stability constants in propylene carbonate and dimethylsulfoxide (*100*) for sodium and silver ions (Table 3.4.1.). Only 1:1 stoichiometry complexes were found for silver and sodium ions (*100*). On the other hand, silver complexes are less stable in dimethylsulfoxide and more stable in propylene carbonate than in water or methanol, which can be explained according to the donor properties of the solvents. As in water and methanol, the authors referred to the existence of a "cryptate effect" in dimethylsulfoxide (*100*).

Cox and coworkers (*50*) measured the stability constants of silver complexes involving open-chain, macrocyclic, and macrobicyclic diaza-polyethers in water–acetonitrile mixtures. Parameters like the dissociation rates of the different complexes, solvation energies of ligands and complexes,

TABLE 3.4.1
Stability Constants of Complexes Involving Cryptands with Silver and Sodium Ions (25°C, indicated solvents, perchlorate medium)

Ligands	Solvent	Ions	log K
	PC	Ag^+	18.80 ± 0.04
		Na^+	12.78 ± 0.04
	DMSO	Ag^+	9.73 ± 0.01
		Na^+	7.24 ± 0.01
	PC	Ag^+	16.33 ± 0.02
		Na^+	10.83 ± 0.02
	DMSO	Ag^+	7.15 ± 0.01
		Na^+	5.28 ± 0.01

solvent composition, and formation rates of the complexes involved were studied in detail (*50*).

Similar determinations were carried out by the same group of authors regarding the comparison between a diaza macrocycle and related cryptand (*101*). They concluded that when there are not specific interactions such as between Ag^+ and nitrogen atoms, the addition of an extra bridge to the monomacrocycle has a strong influence on the stabilities of the complexes, valid for different solvents. This is true for Na^+, K^+, and Tl^+, even though they exhibit an appropriate size for the ligand cavities (*102*).

Cox and coworkers (*9*) measured the stability constants and rates of formation and dissociation of alkaline and silver complexes of monensin (Fig. 3.1.1.1, Section 3.1.1) in ethanol, and compared the results obtained with analogous complexes involving three cryptands. For the particular case of silver, the preformed cavity of the cryptand ligand gives rise to higher stabilities (*9*).

Buschmann measured the silver complex stabilities involving some bicyclic ligands (*87*) by potentiometric titration. In general, the bicyclic complexes are more stable than the related monocycles. Reducing the cavity size of cryptands by introducing benzo rings leads to a small decrease in complex formation. Other structural changes that were tested did not influence the latter parameter (*87*).

The same author extended his study to a variety of noncyclic compounds, crown ethers, azacrown ethers, and cryptands, testing them as complexants of the silver ion in methanol (*7*). Using potentiometric and calorimetric titrations, Buschmann concluded that a "cryptate effect" takes place in the complexation of silver, explained by an increase in the respective reaction enthalpy. In reverse, there is not a "macrocyclic effect" due to the possibility of different conformations which can be adopted by the cyclic ligands (*7*).

Kumegai and Akabori (*126*) synthesized the cryptand derivatives illustrated in Fig. 3.4.2. They found that the extraction ability showed by these ligands toward silver is reasonable according to the experimental conditions used (*126*). Nevertheless, there is a significant percentage of extraction for the alkaline and alkaline-earth metal cations under the same experimental conditions.

An extraction study was performed by Izatt and coworkers (*71*) involving this type of ligands and silver and lead ions (Table 3.4.2). According to the authors, the addition of acidic extractants to neutral macrocycles increases cation extraction from salt solutions containing "hard" anions such as NO_3^- or Cl^-, because their presence in the organic phase allows an easier exchange of protons for cations (*71*). Thus, they verified that the addition of D_2EHPA, bis-(2-ethylhexyl)-phosphoric acid, increases the extraction

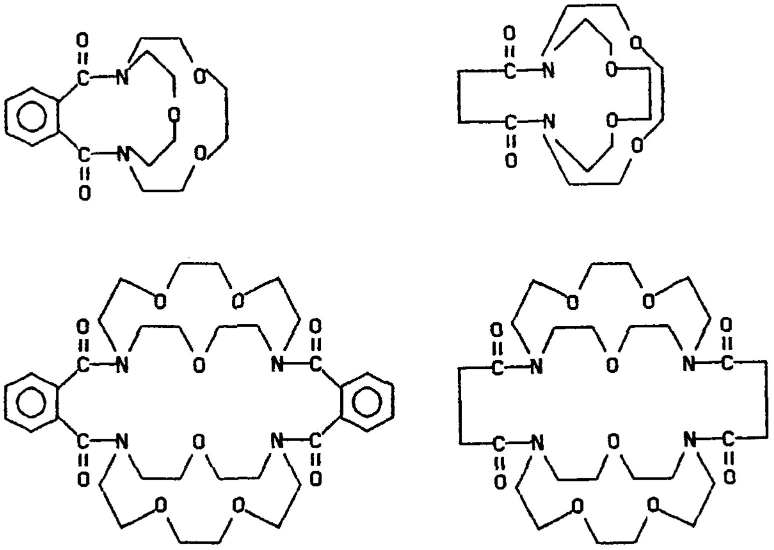


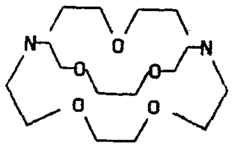
FIG. 3.4.2. Cryptand derivatives used for the extraction of several metal ions (metal nitrates, dichloromethane, picrate medium).

of both silver and lead ions ($D_{Ag^+} = 0.51 \pm 0.1$ and $D_{Pb^{2+}} = 9.92 \pm 1.33$) for the same experimental conditions as given above.

Cryptands were also used as cation carriers in some transport studies involving liquid membranes (*113, 127, 128*). Considerations concerning their transport efficiency, together with the selectivity showed to silver, will be referred in the next section.

In conclusion, cryptands do not seem to be promising ligands for the selective extraction of silver.

TABLE 3.4.2
Distribution Coefficients and Stability Constants of the Ligand with Silver and Lead Ions (25°C, water/toluene, nitrate medium)

Ligand	D	log K
	Ag^+ – 0.02 ± 0.03	10.16
	Pb^{2+} – 0.20 ± 0.04	13.13

3.5. Transport of Silver through Liquid Membranes

The main work on this subject has been done by two groups of researchers: the R. M. Izatt group (*128–134*) and the Japanese group of Tsukube and coworkers (*10, 113, 127, 135, 136*).

Crown ethers have been widely used as cation carriers through liquid membranes. Their selectivity to silver has been compared to that shown by the analogous macrocycles containing S- and N-donor atoms, as well as with that of cryptands and naturally derived antibiotic macrocycles like valinomycin and monensin. Thus, Izatt and coworkers measured the rates of transport of the nitrate salts of the alkaline, alkaline-earth, silver, and lead cations by using a large number of macrocyclic ligand carriers (*128*). They found that transport selectivity was observed for those cations that best fit the ligand cavity as long as the complex stability constant did not exceed certain values. Another important feature they verified is that the open-chain compound, analogous to the crown ethers studied by them were ineffective as cation carriers: in addition, there was not a significant change in transport rates or selectivities through the introduction of large aliphatic groups to crown ethers and cryptands with the aim of minimizing losses of carriers to the water phases (*128*).

The transport of Pd^{2+} by different sulfur-substituted macrocycles was extensively studied (*129*). The authors used a 1.5 M $HNO_3/CHCl_3$/0.01 M HNO_3 bulk liquid membrane to evaluate the competition in different binary systems including Pd^{2+} (Table 3.5.1). A curiosity of this study is that the

TABLE 3.5.1
Flux Values of Two Binary Systems (J_M = mol·s^{-1}·m^2 × 10^{-8}) through a $HNO_3/CHCl_3/HNO_3$ Bulk Liquid Membrane

Ligands	Cations	Flux values
18C6	Pd^{2+}/Ag^+	0/189
	Pd^{2+}/Pb^{2+}	0.1/289
T18C6	Pd^{2+}/Ag^+	58/8
	Pd^{2+}/Pb^{2+}	39/7
$T_2$18C6	Pd^{2+}/Ag^+	52/2
	Pd^{2+}/Pb^{2+}	52/2
$T_6$18C6	Pd^{2+}/Ag^+	0.1/2
	Pd^{2+}/Pb^{2+}	0/0.2

cation fluxes of Ag^+ and Pb^{2+} in single-salt systems are much greater than that of Pd^{2+}. The inverse situation occurs in the corresponding binary systems (*129*). The interpretation of this fact (*129*) is not very clear.

The same group of authors described a method for the separation of Ag^+ from Pb^{2+} by using pyridono- and triazolo-type macrocycles (*130*). Cation transport by macrocycles is often diffusion limited, so such parameters as the extraction constants, distribution coefficients, aqueous phase macrocycle–cation, and anion–cation interaction constants, must always be considered, as well as the membrane geometry. Thus, the influence of the macrocycle type, solvent, cation, and anions in the latter parameters is examined. The mechanisms involved in the transport of cations are also discussed (*130*).

The selective transport of Ag^+ over other metals in competitive experiments by the proton-ionizable pyridone and triazole types was studied in detail (*131*). In terms of the mechanisms involved, the transport by pyridone macrocycles includes the co-transport of an anion. The same is not totally true when triazole-type macrocycles are used, where either co-anion transport or counter-transport of a proton can occur (*131*). According to the authors, the highly selective transport of silver over lead and thallium with triazolo-18-crown-6 is mainly due to the affinity showed to this cation by the triazole moiety, to the good fit of the cation with the 18-crown-6 cavity, and to the presence of only one proton-ionizable site per macrocycle (*131*).

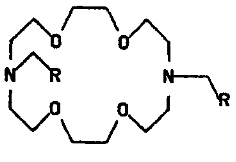
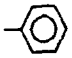
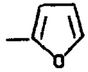
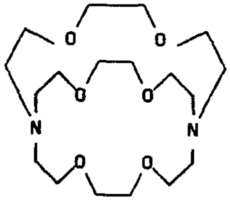
Previous work by the same group of authors pointed out that the selection of macrocycles having a proper cavity ratio and appropriate combinations of oxygen with either nitrogen or sulfur atoms led to selective transport of silver in binary cation systems using a $H_2O–CHCl_3–H_2O$ liquid membrane type (*132*). The macrocycles studied, derivatives of diketo-pyridine-18-crown-6, showed, however, a few exceptions in the selectivity in some experiments, preferentially transporting lead and thallium (*132*).

Izatt and coworkers also studied the transport of Cd^{2+} in the presence of Ag^+ by different types of emulsion membranes (*133, 134*). By using the thiocyanate salts of both cations as the aqueous phase, dicyclohexane-18-crown-6 as the carrier dissolved in toluene, and a receiving phase containing nitrate salts of Mg^{2+}, they found a rapid transport of Cd^{2+} over Ag^+ due to a more favorable formation of neutral complexes of the former cation compared to the latter (*134*).

In addition to the extraction properties of different aza macrocycles with ligating donor atoms toward several cations, Tsukube and coworkers also studied their transport characteristics (*113, 135*). By using a chloroform or a dichloromethane liquid-membrane system, they found the results listed in Table 3.5.2. Derivatives of diaza crown ethers with furan and thiophene

TABLE 3.5.2

Transport Properties of Double Armed diaza-crown-ethers and a Cryptand (perchlorate medium, carrier in chloroform, water as receiving phase). (The asterisk indicates Ag(0) deposited on the wall of the transport cell)

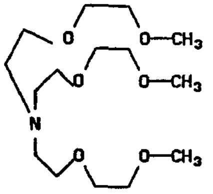
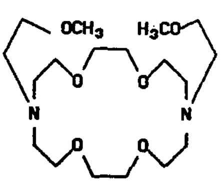
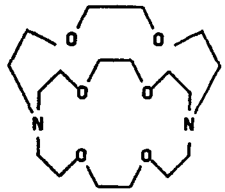
Ligands	R	Transport rate . 10^6(mol/h)			
		Na^+	K^+	Ag^+	Pb^{2+}
		< 0.3	0.97	1.82	9.09
		0.78	7.52	1.68	8.17
		< 0.3	2.59	*	16.00
		6.54	1.21	2.02	1.63

moieties showed characteristic transport properties which were significantly different from those of the simple crown ether and the cryptand (*113*). In fact, the transport properties showed by the former ligands seem to be determined by the size of the parent diaza crown ring, but the nature of the ligating donor arm groups also affected the transport characteristics.

More recently, the same authors reported that "tripod-type host" molecules, due to their more flexible nature than the similar double-armed diaza macrocycles, offer a unique and specific transport of silver ion by a three-dimensional complexation process (*127, 136*). The results obtained with a ligand of this type, together with a cryptand and a related double-armed diaza macrocycle, are summarized in Table 3.5.3. As can be seen, the tripod showed effective and specific cation transport properties for silver and lead ions over the alkaline cations (*127*).

More specific diaza crown ether derivatives were also recently tested as cation carriers (*106*). Some of the results obtained are listed in Table 3.5.4. The selectivity showed by the first ligand in the table toward silver seems remarkable (*106*). Syntheses of more complicated diaza crown ether derivatives by particular high-pressure tactics for possible application as specific host molecules are in progress (*106*).

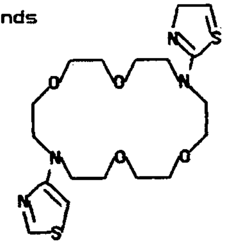
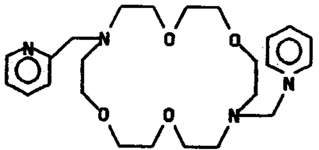
TABLE 3.5.3
Transport Properties of a Tripod and Other Host Molecules (chloroform liquid membrane system, perchlorate medium, water as receiving phase)

Ligands	Transport rate . 10^6 (mol/h)			
	Na^+	K^+	Ag^+	Pb^{2+}
	0.0	0.2	6.5	1.8
	4.8	9.8	0.8	1.7
	6.5	1.2	2.0	1.6

Tsukube and Sohmiya (*10*) used the methyl ester of monensin (see Fig. 3.1.1.1, Section 3.1.1) as the silver carrier in a liquid membrane system. For the set of experimental conditions used, the authors concluded that Ag^+ (transport rate 4.8×10^{-6} mol·h^{-1}) and Na^+ (transport rate 0.7×10^{-6} mol·h^{-1}) were the only cations transported over the alkaline, alkaline-earth, ammonium, and lead ions (*10*).

^{13}C-NMR spectroscopy was used to evaluate the cation-binding properties of the ligand, and the spectral changes obtained upon complexation with silver indicate that the pseudo-cyclic monensin skeleton encases Ag^+ by using the polyether chain and terminal ester moiety (*10*). Structural differences between the silver and sodium complexes, detected by the above-mentioned type of spectroscopy, seem to be reflected in the transport profile of the ligand (*10*).

TABLE 3.5.4
Flux of Cations from a Source Phase in Perchlorate Medium for a Dichloromethane Phase Containing the Indicated Ligands. Water as Receiving Phase. The Dashes Indicate Values below the Limit of Detection

Ligands	Transport rate . 10^6 (mol/h)			
	Na^+	K^+	Ag^+	Pb^{2+}
	–	–	4.9	–
	10.5	7.9	–	3.2

Cho and coworkers (*137*) used different aza macrocycles as cation carriers by using a bulk liquid membrane system. Studies on single cation transport showed that the best macrocyclic ligand for transport is the one which forms a moderately stable rather than a very stable complex during extraction. However, for double cation transport, it was seen that the cation which forms the most stable complex with the carrier is favored over the other cations (*137*).

The transport of ions through liquid membranes is a well-elaborated method containing several specific details which can be critically controlled to simplify interpretation of the phenomena involved. As a result, this method must not be followed if the extraction properties of the ligands being studied are not well known. An additional problem of transport is the simultaneous optimization of the receiving aqueous phase, which is not always easy. Nevertheless, the method is interesting, and the constant renewal of the conception of membrane-type systems motivates its applicability.

This review shows that much work must be done to clarify the chemical processes related to the extraction phenomena. Some attempts to explain one or another particular case of extraction have been successful. Nevertheless, a new approach seems to be necessary for an effective and general contribution to the development of the solvent extraction phenomenon itself, and that approach should focus on features related to the liquid–liquid interface.

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