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Abstract: Two new macrocyclic Schiff bases, (**5**) and (**7**), containing nitrogen-sulfur donor atoms were designed and synthesized by reaction of α,α' bis(o-aminophenylthio)-1,2-xylene with glyoxal and phthaldialdehyde, respectively. The liquid-liquid extraction of metal picrates such as Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, K^+, and Na^+ from aqueous phase to the organic phase was carried out using the novel ligands. The effect of chloroform and dichloromethane as organic solvents over the metal picrate extractions was investigated at $25 \pm 0.1°C$ by using UV-visible spectrometry. The extractability and selectivity of the tested metal picrates were evaluated. The values of the extraction constants ($\log K_{ex}$) were determined for the extracted complexes.

Keywords: N_2S_2-macrocycle, solvent extraction, transition metal cation

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INTRODUCTION

The key to an efficient separation process is the development of an extractant with a strong preference for relevant chemical species. Examples of such extractants include macrocyclic ligands, called crown ethers that bind metal ions such as sodium, potassium, lithium, cesium, strontium, and barium (1–4). An appropriate macrocyclic ligand exhibits good extraction selectivity for desired metal ion species. Recently, a crown extractant was used in the solvent extraction process for separating radioactive ^{137}Cs from the high- level wastes. Technetium is another element removed from alkaline nuclear-waste solution by the use of crown ethers.

Crown ethers were also used as spectrophotometric analytical reagents. For example, the use of some crown ethers for the measurement of lithium in biological samples have been reported (5). Metal ions have enormous importance in many biological processes. Especially, heavy metal ions are effective enzyme inhibitors exerting toxic effects on living systems (6). Therefore, separation and determination of toxic metal ions such as mercury, lead, and cadmium in environmental sources play an important role for healthy life. Although the using of crown ethers in determination and separation of alkali metals has been thoroughly investigated, their usage as extractants for the mentioned toxic metals has relatively received little attention (7, 8).

Firstly, Pedersen tried to extract alkali metal picrates by using crown ethers with oxygen donor, from aqueous solution into dichloromethane and showed the close relationship between the crystal radii of alkali metal ions and the size of the cavity of crown ethers (9). This concept, which is known as a structural match, is the simplest approach in the effective and selective extraction of alkali and alkaline-earth metals with crown ethers. But the principle of structural match generally is not valuable for transition metal ions. Oxygen-containing crown ethers extract most of the transition metals poorly, whereas nitrogen-and sulfur-containing macrocycles can extract such metal ions as selective (10).

Although the macrocyclic compounds are mainly the oxygen, nitrogen, and sulfur types, the macrocyclic compounds used in solvent extraction were mostly of the oxygen type. However, Lindoy and Meehan have reported the use of some tri-linked N_2S_2 macrocycles without aromatic moieties as well as with their corresponding single ring analogs as ionophores in membrane transport experiments involving transition metal ions such as Cd^{2+}, Ag^{+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, and Co^{2+} (11).

Our recent work has focused on the use of $N_2O_2S_2$ macrocycles containing aromatic moieties for the transfer of various metal ions from the aqueous phase into the organic phase in liquid-liquid extraction systems (12). We were interested in the design and synthesis of two novel N_2S_2-crown ether extractants for the selected metal ions, which have smaller cavity size than those of the former. The aim of this investigation was to elucidate the effect of mixed donors and the structural match between cavity of ligand and metal size on the extraction of transition metal ions.

EXPERIMENTAL

Reagents and Apparatus

Chloroform, dichloromethane, picric acid, $Hg(NO_3)_2 \cdot H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6\ H_2O$, $Ni(NO_3)_2 \cdot 6\ H_2O$, $Cd(NO_3)_2 \cdot 4\ H_2O$, $Mn(NO_3)_2 \cdot 4\ H_2O$, $NaNO_3$, $AgNO_3$ and KNO_3 were the analytical grade reagents and were purchased from Merck. 2-Aminothiophenol, α,α'-Dibromo-o-xylene, glyoxal, and phthaldialdehyde were obtained from Fluka. Demineralized water was used in extraction experiments. The solvents were saturated with each other before use in order to prevent volume changes of the phases during extraction.

^1H and ^{13}C-NMR spectra were recorded at ambient temperature on a Varian Mercury-200 spectrometer using $CDCl_3$ with TMS as the internal standard. IR spectra were obtained on a Perkin –Elmer 1600 FT-IR spectrometer with the samples in compressed KBr discs. Mass spectra of the ligand was measured on a Micromass Quattro LC-MS/MS spectrometer. An Orion Research Model 601 Digital Ionalyzer was used for adjusting the pH of alkaline metal picrate solutions. The spectrophotometric measurements were carried out with Unicam UV2 UV-visible spectrophotometer. In solvent extraction experiments Grant SS 30 type shaker with thermostat was used.

Synthesis of 5,6; 9,10; 13,14- tribenzo-1,4-diaza-7,12-dithiacyclotetradecane-1,4-diene (5) α,α' Bis(o-aminophenylthio)-1,2-xylene **3** (13) (1.00 g, 2.84 mmol) was dissolved in ethanol (250 mL) and purged under nitrogen atmosphere in a Schlenk system connected to a vacuum line. A solution of glyoxal **4** (0.19 g, 2.84 mmol) in ethanol (50 mL) was added dropwise to this solution for 30 min at 25°C. The reaction mixture was refluxed and stirred at reflux temperature for 48 h monitored by TLC [silica gel (chloroform:methanol) (1:1)]. At the end of this period, the solid product was filtered off, washed with hot ethanol and cold diethyl ether, and then dried *in vacuo*. The solid product (0.52 g, 49.05%) was obtained by recrystallization from ethanol, mp 119–120°C. IR (KBr pellets, cm^{-1}): 3043 (Ar–H), 2983–2923 (C–H), 1643 (C=N). ^1H-NMR ($CDCl_3$): (δ) 8.10 (s, 2H, CH=N), 6.61–7.75 (m, 12H, Ar–H), 4.45 (s, 4H, $S-CH_2$). ^{13}C-NMR ($CDCl_3$): (δ) 159.04, 136.61, 135.74, 130.22, 128.04, 127.29, 124.40, 118.85, 117.44, 114.18, 30.62. MS (EI): m/z = 374.1 $[M]^+$.

Synthesis of 3,4; 7,8; 11,12; 15,16-tetrabenzo-1,4-diaza-8,14-dithiacyclohexadecane-1,5-diene (7) α,α' Bis(o-aminophenylthio)-1,2-xylene **3** (1.05 g, 2.98 mmol) was dissolved in ethanol (250 mL) and purged under nitrogen atmosphere in a Schlenk system connected to a vacuum line. A solution of phthaldialdehyde **6** (0.4 g, 2.98 mmol) in ethanol (50 mL) was added dropwise to this solution to for 30 min at 25°C. The reaction mixture was refluxed and stirred at reflux temperature. After a while, the solution turned cloudy and then the yellow solid product precipitated. The reaction was monitored by using TLC [silica gel (chloroform:methanol) (1:1)]. At the end of 24 h, the yellow solid product was filtered off, washed with hot ethanol and cold diethyl ether then dried *in vacuo*. The pale yellow solid product (0.69 g, 51.49%) was obtained by recrystallization from ethanol, mp 156–157°C. IR (KBr pellets, cm^{-1}): 3042 (Ar–H), 2853 (C–H), 1644 (C–N). ^{1}H-NMR ($CDCl_3$): (δ) 7.91 (s, 2H, CH=N), 6.42–7.80 (m, 16H, Ar–H), 4.70 (s, 4H, S–CH_2). ^{13}C-NMR ($CDCl_3$): (δ) 158.50, 136.64, 135.78, 135.12, 130.83, 129.55, 128.75, 128.01, 127.73, 126.80, 126.48, 125.57, 33.99. MS (EI): $m/z = 450.9\ [M]^+$.

Solvent Extraction

Extraction experiments were performed according to the published procedure (12). Transition metal picrates were prepared by the stepwise addition of a 1×10^{-2} M of metal nitrate solution to a 1.25×10^{-5} M aqueous picric acid solution and shaking at 25°C for 1 h. The alkali metal picrates were prepared by stepwise addition of a 0.1 M aqueous solution of metal hydroxide to 25 mL of a 1.0×10^{-3} M aqueous picric acid solution until neutralization, which was checked by pH control with a glass electrode and the solution was dilued to 1.25×10^{-5} M.

An organic solution (10 mL) of ligand (1.25×10^{-4} M) and an aqueous solution (10 mL) containing metal picrate (1.25×10^{-5} M) were placed in stoppered flask, and shaken for 2 h at 25 ± 0.1°C. The resulting mixtures were allowed to stand for at least 2 h at that temperature in order to complete the phase separation. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically at 355 nm. Blank experiments showed that no picrate extraction occurred in the absence of the ligand. The extractability was determined based on the absorbance of picrate ion in the aqueous solutions. The extractability was calculated from Equation (1).

$$E(\%) = [(A_0 - A)/A_0] \times 100 \qquad (1)$$

where A_0 is the absorbance in the absence of ligand. A denotes the absorbance in the aqueous phase after extraction.

The dependence of the distribution ratio D of the cation between the aqueous phase and the organic phase upon the ligand concentration was examined. The range of the ligand was from 2.5×10^{-6} to 1.25×10^{-4} M.

The general extraction equilibrium is assumed to be given by Equation (2).

$$M^{n+}_{aq} + n\ Pic^-_{aq} + m\ L_{org} \rightleftharpoons [M(Pic)_n(L)_m]_{org} \qquad (2)$$

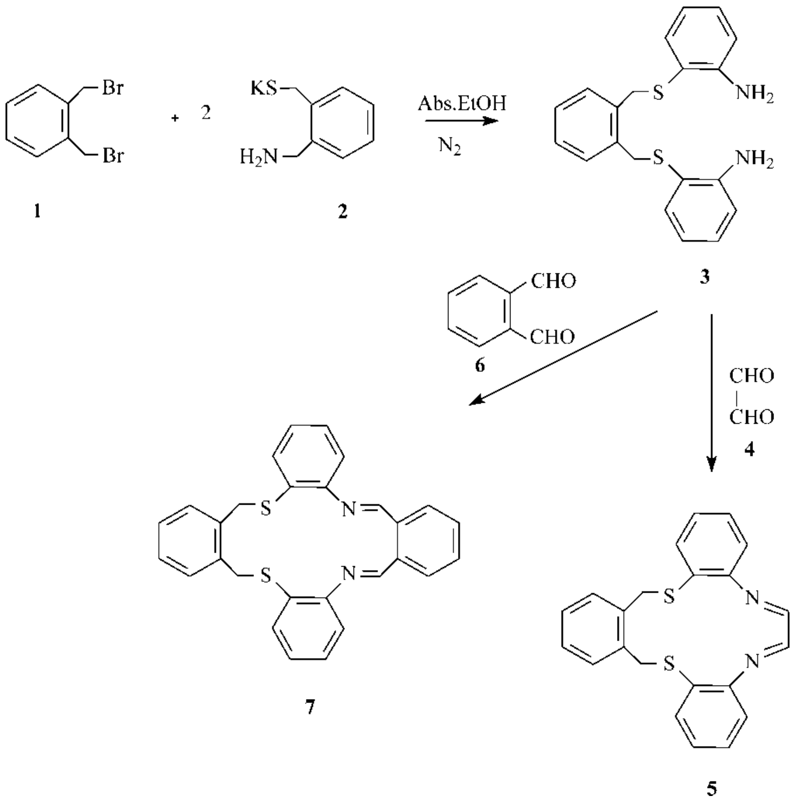
Where the subscript "aq" denotes aqueous solution and the subscript "org" denotes organic solution. The following logarithmic expression is valid for the above extraction system (12).

$$\mathrm{Log\,D} = \mathrm{n\ log\,[Pic]} + \log \mathrm{K_{ex}} + \mathrm{m\,log\,[L]} \qquad (3)$$

The extraction equilibrium constant ($\log \mathrm{K_{ex}}$) between an aqueous solution of metal picrate and an organic solution of crown ether for crown ether-cation complex can be calculated from Equation (3) and from the result shown in Fig. 2.

RESULTS AND DISCUSSION

The synthetic pathways to intermediate (**3**) and new macrocyclic ligands (**5**) and (**7**) are summarized in Scheme 1. α,α' bis(o-aminophenylthio)-1,2-xylene (**3**) was prepared according to the previous paper (13). This compound was characterized by means of IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopies.



Scheme 1. The synthetic pathways to the crown ethers used in the present study.

Compound (**5**) was synthesized by reaction of α,α' bis(o-aminophenylthio)-1,2-xylene (**3**) with glyoxal (**4**) in ethanol under high dilution conditions in a Schlenk system. The difference between the IR spectra of (**3**) and (**5**) is clear by the absence of characteristic vibration, at 3415–3350 cm^{-1} belonging to the NH_2 groups. In addition, the stretching vibrations at 1643 cm^{-1}, confirms the presence of imine groups. In the ^{1}H-NMR spectrum of (**5**), there is a singlet at $\delta = 8.10$ ppm for the protons of azomethine groups indicating the formation of a Schiff base. The absence of the singlet at $\delta = 5.23$ ppm belonging to the primary aromatic amine groups of the starting material supports the formation of the compound (**5**). More detailed information about the structure of compound (**5**) is provided by its ^{13}C-NMR spectrum. The carbon resonance of azomethine groups is found at $\delta = 159.0$ ppm. On the other hand, the mass spectral analysis of (**5**), which shows a molecular ion peak at $m/z = 374.1$ $[M]^+$, confirms the proposed structure.

Compound (**7**) was obtained by the reaction of α,α' bis(o-aminophenylthio)-1,2-xylene (**3**) with phthaldialdehyde (**6**). The conditions of synthesis of this compound are very similar to those of compound (**5**). Spectroscopic data of (**7**) clearly confirmed the success of the macrocyclization.In the IR spectrum of compound *(7)*, the C=N stretching vibration was observed at 1641 cm^{-1} as a strong absorption. The absence of primary aromatic amine groups belonging to compound (**3**) and carbonyl groups belonging to compound (**6**) has also supported the macrocyclization. In the ^{1}H-NMR spectrum of (**7**), the chemical shifts belonging to HC=N protons at $\delta = 7.91$ ppm, appeared after the macrocyclization reaction. The absence of the singlet at $\delta = 5.23$ ppm belonging to primary aromatic amine groups of the starting material, supports the formation of compound (**7**). ^{13}C-NMR spectral data are also in good agreement with this structure. The result of the mass spectral data at $m/z = 450.9$ $[M]^+$ confirms the formation of compound (7).

Extraction of Metal Picrates

Table 1 shows the extractability of Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, K^+, and Na^+ picrates from the aqueous phase into the organic phase by compound (**5**) and compound (**7**). It is clear that the extractability results of the ligands are different for both of the organic solvents. When dichloromethane was used as organic solvent, compound (**5**) extracted Ag^+ ion 65.0 % but the other metal ions were not extracted effectively. Compound (**7**) extracted Ag^+ ion 94.4% for the same solvent. It is interesting that the percentage of the extraction of all the metal ions with compound (**7**) is higher than that of compound (**5**) for both of the solvents. These results suggested that the benzen group is the efficient group in the extraction. However, it can be seen from Table 1 that the solvent has an important effect upon the cation

Table 1. The extractability of aqueous metal picrates for compound (**5**) and (**7**) into organic phase[a]

	Extractability[a,b] (%)		Extractability[a,c] (%)	
Metal ion	(**5**)	(**7**)	(**5**)	(**7**)
Ag^+	65.0 ± 0.8	94.4 ± 1.1	7.5 ± 1.4	79.5 ± 1.2
Hg^{2+}	14.8 ± 0.6	61.2 ± 1.3	3.1 ± 0.7	57.8 ± 1.0
Cd^{2+}	0.5 ± 0.1	31.9 ± 0.8	0.3 ± 0.1	22.6 ± 1.3
Zn^{2+}	4.5 ± 0.1	8.7 ± 0.3	1.3 ± 0.1	16.4 ± 1.1
Cu^{2+}	6.0 ± 0.2	46.8 ± 0.7	0.6 ± 0.1	44.0 ± 0.7
Ni^{2+}	5.1 ± 0.1	20.3 ± 0.5	0.9 ± 0.2	17.7 ± 0.5
Mn^{2+}	2.0 ± 0.1	24.5 ± 0.6	0.5 ± 0.1	36.4 ± 0.6
K^+	0.6 ± 0.1	12.4 ± 0.3	3.1 ± 0.5	12.5 ± 0.3
Na^+	4.2 ± 0.3	23.0 ± 0.8	5.6 ± 0.4	46.3 ± 0.9

[a] Temperature: 25.0 ± 0.1°C; aqueous phase (10 mL); $[pic^-] = 1.25 \times 10^{-5}$ M, organic phase (10 mL); $[L] = 1.25 \times 10^{-4}$ M; The values and standard deviations calculated from three independent extraction experiments.

[b] Defined as percent picrate extracted into dichloromethane phase.

[c] Defined as percent picrate extracted into chloroform phase.

extractability. These results may depend on dielectric constants of the solvents. The dielectric constants of dichloromethane and chloroform are 9.1 and 4.8, respectively. Dichloromethane having a high dielectric constant is favored for the extraction of all the metals. There are similar results in the literature (14). On the other hand, the better solvation of the complexes by dichloromethane may be a valuable reason for better extraction. Compound (**5**) exhibited the lowest extraction efficiency for all the metal ions, when chloroform was used as solvent. In this case, all the metals were extracted less than 7.5% with compound (**5**). The best extractability belongs to Ag^+ ion but it is only 7.5%. Whereas the extractability for Ag^+ reaches 79.5% with compound (**7**) in chloroform. This difference may be resulting from the lipophilicity of the metal-compound (**7**) complex.

From the extraction data shown in Table 1 it is clear that the ligands which have N_2S_2 donor set shows generally an pronounced ability to bind an Ag^+ ion. However, the macrocycle used in the previous work (Fig. 1) has $N_2O_2S_2$ donor atom set and it also transfers Ag^+ ion into chloroform phase 65.4% (12). These results show that both the ion-cavity size and the type of binding sites in the ring contribute to the ability of Ag^+ ion binding. In this study the best extractability for Ag^+ ion belongs to compound (**7**) which has molecular symmetry in comparison to the other ligands. This may be shown as the most effective property in cation transfer in relation to explain our extraction results. There are similar results for ligands with nitrogen-oxygen mixed donor in the literature (15).

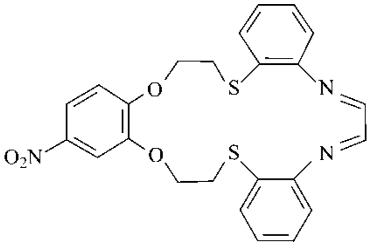


Figure 1. Structure of the crown ether used in the previous work.

Table 2 shows the selectivity of silver picrate over the other metal picrates for the ligands. The selectivity is indicated as $D_{Ag+}/D_{M^{n+}} \cdot D_{Ag+}$ and $D_{M^{n+}}$ denotes the distribution ratio of Ag^+ ion and M^{n+} ion, respectively. Both compound (**5**) and compound (**7**) indicated high selective extraction of Ag^+ ion over the other metal ions. However, the selectivity results for dichloromethane are higher than those for chloroform. When dichloromethane was used as organic solvent, compound (**5**) showed highest selectivity for Ag^+ ion over Cd^{2+} and K^+ ions with 376.6 and 269.0, respectively. Similarly, compound (**7**) extracted Ag^+ ion as selective over Zn^{2+} and K^+ ion with 179.68 and 121.06, respectively. Also, the extraction experiments with compound (**7**) in which chloroform was used as organic solvent gave the best selectivity for Ag^+ ion over K^+ ion among the tested metal cations. The selectivity of Ag^+/K^+ is 35.92 in this case.

In order to determine the composition of extracted complexes, the effect of changing ligand concentration over the distribution ratio at constant

Table 2. The selectivity of silver picrate over the other metal picrates for compound (**5**) and (**7**)

	Selectivity[a,b] Ag^+/M^{n+}		Selectivity[a,c] Ag^+/M^{n+}	
Metal ion	(**5**)	(**7**)	(**5**)	(**7**)
Hg^{2+}	10.9	11.3	1.97	2.83
Cd^{2+}	376	36.5	25.0	3.37
Zn^{2+}	40.9	179	5.77	19.5
Cu^{2+}	29.9	19.4	12.5	4.96
Ni^{2+}	35.5	67.2	8.33	18.1
Mn^{2+}	94.2	52.4	15.0	6.80
K^+	269	121	2.34	35.9
Na^+	43.8	59.5	1.33	4.49

[a] Defined as D_{Ag+}/D_M^{n+}, where D_{Ag+} and D_M^{n+} represent the distribution ratio of Ag^+ ion and M ion, respectively.

[b] Calculated for dichloromethane as organic solvent.

[c] Calculated for chloroform as organic solvent.

picrate concentration was investigated. The plot of log $\{D/[Pic^-]^n\}$ as a function of log [L] should give a straight line with a slope of m and log K_{ex} can be calculated from the intercept by using Equation (3).

The composition of extracted complexes for compound (**7**) and their log K_{ex} values for chloroform as organic solvent were given in Table 3. We can see the relationship between the complex composition and corresponding ionic diameters from Table 3. Compound (**7**) gives the 1:1 complexes for Hg^{2+}, Na^+ and Cd^{2+} having close ionic diameters. However, the complexes of compound (**7**) with Ag^+ and K^+ have the 2:1 (L:M) composition. These results show that the 16-membered macrocycle gives the sandwich complexes with Ag^+ and K^+ ions. As seen from Table 3, the highest log K_{ex} values belong to Cd^{2+}, Zn^{2+}, Mn^{2+}, Cu^{2+} and Hg^{2+} ions with 14.73, 14.46, 13.87, 13.74 and 13.61, respectively. These results can be explained with HSAB concept. Especially, Cd^{2+} and Hg^2 ions are known as soft metal cations and prefer nitrogen and sulfur donor atoms in complexation with macrocycles. Consequently, the high log K_{ex} values may result from the stability of the mentioned complexes. The efficiency of extraction of alkali and alkaline-earth metal cations with known crown ethers, which can be characterized by the extraction constant, is controlled by the stability of the complex (10). Our results show that a similar approach may be valid for transition metal cations with N_2S_2 macrocycles.

The results of the experiments at different concentrations of crown ethers but constant picrate concentration revealed the 1:1 composition for Hg^{2+} while the 2:1 composition for Ag^+ ion, when dichloromethane is used as organic solvent (Fig. 2). These results of complex composition are similar to those of chloroform for these ions (Table 3).

Table 3. The relationship between composition, extraction constant and ionic diameter for the cation-compound (**7**) complexes.

Metal ion	Extraction constant (log K_{ex})[a]	Complex composition (L:M)	Ionic diameter (A°)
Ag^+	11.35	2:1	2.52
Hg^{2+}	13.61	1:1	2.20
Cd^{2+}	14.73	1:1	1.95
Zn^{2+}	14.46	1:1	1.66
Cu^{2+}	13.74	1:1	1.64
Ni^{2+}	11.53	1:1	1.50
Mn^{2+}	13.87	1:1	1.62
K^+	13.52	2:1	2.66
Na^+	10.47	1:1	1.94

[a] Used chloroform as organic solvent.

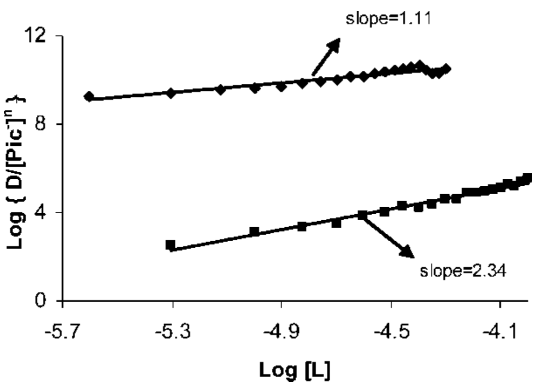


Figure 2. Log{D/[Pic$^-$]^n} versus log[L] for the extraction of Hg-picrate (◆) and for Ag-picrate(■). L: compound (**7**), organic solvent: dichloromethane.

CONCLUSION

The high transfer of Ag^+ ion from the aqueous phase to the dichloromethane phase was observed with compound (**7**). It is found that both 16-membered N_2S_2 macrocycle (**7**) and 14-membered N_2S_2 macrocycle (**5**) extract Ag^+ ion compared to the other transtion metal cations as selective. The composition of extracted Ag-complexes was 2:1 (L:M) for both of the ligands.

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REFERENCES

1. Takeda, Y., Takagi, C., Nakai, S., Endo, K., and Katsuta, S. (1999) Extraction of sodium and potassium picrates with 16-crown-5 into various diluents. Elucidation of fundamental equilibria determining the extraction selectivity for Na^+ over K^+. *Talanta*, 48: 559.
2. Tong, A.J., Song, Y.S., Li, L.D., et al. (2000) Selective extraction of alkali metal cations with proton-ionizable dibenzo-16-crown-5 fluorophores. *Anal. Chim. Acta*, 420: 57.
3. Tsurubou, S., Mizutani, M., Kadota, Y., et al. (1995) Improved extraction-separation of alkaline earths and lanthanides using crown ethers as ion size selective masking reagents: A novel macrocycle application. *Anal. Chem.*, 67: 1465.
4. Walkowiak, W., Brown, P.R., Shukla, J.P., and Bartsch, R.A. (1987) Selective separation of alkali metal cations by bulk chloroform membranes containing lipophilic crown ether phosphonic acid monoethyl esters. *J. Membrane Sci.*, 32: 59.

5. Christian, G.D. (1996) Analytical strategies for the measurement of lithium in biological samples. *J. Pharm. Biomed. Anal.*, 14: 889.
6. Bacon, E. and Kirch, M. (1987) Competetive transport of the toxic heavy metals lead, mercury and cadmium by macrocyclic ligands. *J. Membrane Sci.*, 32: 159.
7. Sekido, E. and Nakabayashi, A. (1989) Liquid/liquid extraction of metal ions with a polythioether derivative in its reduced bismercapto form or its oxidized disulphide form. *Anal. Chim. Acta*, 221: 99.
8. Aguilar, J.C., San Miguel, E.R., Gyves, J., et al. (2001) Design, synthesis and evaluation of diazadibenzocrown ethers as Pb^{2+} extractants and carriers in plasticized cellulose triacetate membranes. *Talanta*, 54: 1195.
9. Pedersen, C.J. (1970) Crystalline salts complexes of macrocyclic polyethers. *J. Amer. Chem. Soc.*, 92 (2): 386.
10. Beklemishev, M.K., Dmitrienko, S.G., and Isakova, N.V. (1997) Solvent extraction of metals with macrocyclic reagents and its analytical applications. In *Macrocyclic Compounds in Analytical Chemistry*; Wiley-Interscience: New York.
11. Chartres, J.D., Groth, A.M., Lindoy, L.F., and Meehan, G.V. (2002) Metal ion recognation. Selective interaction of silver (I) with tri-linked N_2S_2-donor macrocycles and their single-ring analogues. *J. Chem. Soc. Dalton Trans.*, 371.
12. Kantekin, H., Ocak, Ü., Gök, Y., and Acar, İ. (2004) The synthesis and characterization of a novel vic-dioxime and its mononuclear complexes bearing an 18-membered $N_2O_2S_2$ macrocycle and their characteristics as extractants for transition metal ions. *J. Inc. Phenom.*, 48: 95.
13. Gök, Y., Karaböcek, S., Karaböcek, N., and Atalay, Y. (1995) The synthesis and characterization of a novel (E,E)-dioximes and their mono- and heteronuclear complexes. *New J. Chem.*, 19: 1275.
14. Saito, K., Taninaka, I., Murakami, S., and Muromatsu, A. (1994) Synthesis of thiacrown ether carboxylic acids and their characteristics as extractants for metal ions. *Anal. Chim. Acta*, 299: 137.
15. Ziyadonogullari, B., Topal, G., Erdogan, S., et al. (2001) Effect of structural modifications of diaza-18-crown-6 on the extractability and selectivity of univalent metal picrates. *Talanta*, 53: 1083.