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Synthesis and Metal-ion Binding Properties of New $N_2S_4O_2$- and $N_2S_5O_2$-Donor Macrocycles

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Abstract: Synthetic procedures for new mixed-donor macrocycle compounds were reported. The macrocyclic compounds were used in solvent extraction metal picrates such as Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Pb^{2+}, and Co^{2+}. The metal picrate extractions were investigated at 25 ± 0.1°C with the aid of UV-visible spectrometry. It was found that 6,7,9,10,12,13,23,24-octahydro-19H,26Hdibenzo[h,t](1,4,7,13,16,22,10,19) dioxatetrathiadiazasiclotetracosine-20,27(21H,28H)-dione showed selectivity towards Ag^+, Hg^{2+}, and Cd^{2+} among the other metals. The extraction constants (Log K_{ex}) and complex compositions were determined for the Ag^+ and Hg^{2+} complexes for this compound and 9,10,12,13,23,24,26,27,29,30-decahydro-5H,15H-dibenzo-[h,w][1,4,7,13,16,19,25-,10,22] dioxapentathiadiazacycloheptacosine-6,16(7H,17H)-dione.

Keywords: Extraction constant, solvent extraction, mixed-donor macrocycle, macrocyclic complex, transition metal ion

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INTRODUCTION

Macrocyclic compounds have been of considerable interest in recent years because of their ability to form remarkably stable and selective complexes with a number of metal ions and of their interesting solubility in some solvents such as chloroform and dichloromethane (1). Macrocycles containing nitrogen/or sulfur donor atoms are of interest as they exhibit high affinities towards heavy transition metal ions, and their selectivity is readily tunable by altering the composition of the donor-atom set or ring size. Mixed N, O, S-donor crowns, therefore, form an interesting class of compounds, which have found use as selective extractants for soft metal cations (2). The availability of mixed donor crowns, however, is often limited by synthetic difficulties and many different approaches have been developed (3).

Firstly, Pedersen tried to extract alkali metal picrates by using crown ethers with oxygen donors from aqueous solution into dichloromethane and showed the close relationship between the crystal ratio of alkali metal ions and the size of the cavity of crown ethers (4). This concept, which is known as structural match, is the simplest approach for the effective and selective extraction of alkali and alkaline-earth metals with crown ethers. But the principle of structural match is generally 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 often selectively (5).

Macrocyclic multidendate ligands with an appropriate combination of ring size, type, and position of donor atoms often exhibit good extraction selectivity for desired metal ions. These compounds have been used successfully for diverse processes such as separation of ions by transport through artificial and natural membranes, liquid-liquid phase-transfer reactions, preparation of ion-selective electrodes and isotope separation (6–10).

In the previous studies, we have investigated solvent extraction properties of some macrocyclic ionophores containing diazadithia, diazatetrathia, and diazapenthia mixed donor atoms for heavy metals (11–13). In this study, we are interested in the design and synthesis of ligands (5), (9), and (11) with nitrogen-sulfur-oxygen mixed donor atoms presented solvent extraction properties for the transition metal cations such as Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, and Pb^{2+}.

EXPERIMENTAL

Reagents and Apparatus

Picric acid, chloroform, dichloromethane, *p*-sulfonyl tosyl chloride, 1,2-ethanedithiol, 2-mercaptoethylsulfide, 2-aminothiophenol, and chloroacetylchloride were obtained from Merck. Acetonitrile, pyridine, diethyleter, NaOH, HCl, Na_2CO_3 and K_2CO_3 were obtained from Fluka. $Pb(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, $AgNO_3$, and $Hg(NO_3)_2 \cdot H_2O$ were the analytical grade metal salt reagents and were purchased from Merck. Demineralized water was used in the extraction experiments. The solvents were saturated with each other before use in order to prevent volume changes of the phases during extraction.

The IR spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer, using KBr pellets or NaCl discs. ^1H and ^{13}C-NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in deuterated $CDCl_3$, DMSO, and chemical shifts were reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. Elemental analysis was determined by a LECO Elemental Analyser (CHNS O932).

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 2-{[2-(2-{2-[(2-aminophenyl)thio]ethoxy}etoxy)ethyl]thio}phenylamine (3)

A mixture of 2-aminothiophenol (7 g, 56 mmol), ethanol (84 mL), and NaOH (5.6 mL) 40% was warmed and stirred under argon atmosphere. Besides, a solution of 1,9-dibromo-3,6-dioksanonan (14) (7.74 g, 28 mmol) in hot ethanol (56 mL) was put into a dropping funnel, and was added drop by drop to that mixture over approximately one hour. This mixture was refluxed for 10 minutes. At the end of the addition, the mixture was maintained at reflux again for 20 hours. The mixture was cooled to room temperature, and filtered. The solvent was removed under reduced vacuum in a rotary evaporator, and then diethyl ether (10 mL) and Na_2CO_3 (30 mL) 5% was added. The ether phase of this mixture was washed several times with distilled water. The extract was dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure to yield the product as an oily purple solid. Yield 7.61 g (74.67%), IR (NaCl disk), (cm^{-1}) 3449–3349 (NH_2), 3061 (ArC-H), 2917–2864 (C-H), 1605 (NH_2), 1102 (O-CH_2). ^1H-NMR ($CDCl_3$), (δ:ppm): 7.42 (d, 2H, ArH), 7.16 (d, 2H, ArH), 7.05 (t, 2H, ArH), 6.70 (t, 2H, ArH), 3.51 (m, 8H, OCH_2), 3.22 (br, 4H, NH_2), 2.95 (t, 4H, SCH_2). ^{13}C-NMR ($CDCl_3$), (δ:ppm): 148.82, 136.41, 129.99, 118.35, 116.93, 114.89, 70.16, 69.65, 34.44. Anal. Calc. for $C_{18}H_{24}N_2O_2S_2$: C, 59.31, H, 6.64, N, 7.68. Found: C, 58.83, H, 6.94, N, 7.55. MS (LC-MS/ms) (m/z): 365 $[M + 1]^+$.

Synthesis of 4-methylN[2({2[2(2{[2({[(4-methylphenyl) sulfonyl]methyl} amino)phenyl]thio}ethoxy) ethoxy]ethyl}thio)phenyl]benzenesulfonamide (5)

A solution of (3) (3.82 g, 10.5 mmol) in pyridine (84 mL) was stirred in an ice bath at (−5, −8)°C under argon atmosphere. Furthermore; *p*-sulfonyl tosyl chloride (2.41 g, 12.7 mmol) in pyridine (43 mL) was placed into a dropping funnel, and was added drop by drop to the mixture over approximately 2 hours. At the end of this period, the orange colored mixture was poured into a mixture of HCl 10% (160 mL) and ice (420 g). This combined mixture was stirred until it reached room temperature. A white precipitate was extracted with 50 mL of chloroform. The extract was dried over anhydrous magnesium sulfate and the solvent was removed under reduced vacuum in a rotary evaporator to give the crude product. Then, 5 mL of diethyl ether was added to this solid, and the mixture was stirred for almost 24 hours. At the end of this period this product was filtered and washed with diethyl ether then and dried in vacuo. The product was crystallized from ethanol to yield a pale yellow solid. Yield: 3.2 g (45.39%), m.p. 89–92°C IR (KBr tablet), (cm^{-1}): 3248 (N-H), 3065 (ArC-H), 2923–2867 (C-H), 1574, 1588, 1391, 1162 (O-CH_2). ^{1}H-NMR ($CDCl_3$), (δ:ppm): 8.18 (s, 2H, NH), 7.65 (t, 2H, ArH), 7.62 (d, 2H, ArH), 7.48 (d, 4H, Tos), 7.42 (d, 4H, Tos), 7.14 (t, 2H, ArH), 7.01 (t, 2H, ArH), 3.43 (t, 8H,OCH_2), 2.81 (t, 4H, SCH_2), 2.18 (s, 6H, CH_3). ^{13}C-NMR ($CDCl_3$), (δ:ppm): 143.85, 139.66, 136.54, 136.08, 130.53, 129.56, 127.33, 124.95, 124.24, 120.41, 70.15, 48.28, 36.52, 21.56. Anal. Calc. for $C_{32}H_{36}N_2O_6S_4$: C, 57.12, H, 5.39, N, 4.16. Found: C, 56.87, H, 5.34, N, 4.46. MS (LC-MS/ms) (m/z): 695 $[M+Na]^+$.

Synthesis of N-(2-{[2-(2-{2-[(2-aminophenyl)thio]ethoxy} ethoxy)ehyll]thio}phenyl)-2 chloroacetamide (7)

A solution of chloroacetylchloride (2.10 g, 18.68 mmol) in dry benzene (42 mL) and Na_2CO_3 (0.48 g, 4.58 mmol) was stirred in an ice-salt bath at ~6°C under an argon atmosphere. A solution of (3) (3.40 g, 9.34 mmol) in dry benzene (84 mL) was added to a dropping funnel and then was added drop by drop to the above mixture over approximately 2 hours. After the addition, the solution at room temperature was stirred overnight. This solvent was removed under reduced vacuum in a rotary evaporator. The product was washed with dry benzene (2 × 10 mL) then washed with diethylether. The white product was recrystallized from hot methanol and the crystals were dried in vacuo. Yield: 3.15 g (65.6%), IR (KBr tablet), 3280 (N-H), 3022 (ArC-H), 2969–2895 (C-H), 1665 (C=O), 1534,1435 (C=C), 1156 (O-CH_2). ^{1}H-NMR ($CDCl_3$), (δ:ppm): 9.20 (s, 2H, NH), 8.51 (d, 2H, ArH), 7.58 (d, 2H, ArH), 7.45 (t, 2H, ArH), 7.23 (t, 2H, ArH). 3.57(s, 4H, O=CCH$_2$Cl) 3.48(t, 8H, OCH$_2$), 2.91 (t, 4H, SCH$_2$). ^{13}C-NMR (CDCl$_3$), (δ:ppm): 164, 22. 139.50, 131.10, 125.66, 123.10, 120.30, 69.20, 68.9, 43.90. Anal. Calc. for $C_{22}H_{26}Cl_2N_2O_4S_2$: C, 51.06, H, 5.02, N, 5.41. Found: C, 50.92, H, 4.87, N, 5.19. MS (LC-MS/ms) (m/z): 539 $[M + Na]^+$, 540 $[M + Na + 1]^+$.

Synthesis of 6,7,9,10,12,13,23,24-octahydro-19H, 26H, dibenzo[h,t][1,4,7,13,16,22,10,19] Dioxatetrathiadiazasiclotetracosine-20,27(21H,28H)-dione (9)

A mixture of (7) (0.517 g, 1 mmol), 1,2-ethanedithiol (0.94 g, 1 mmol), and K$_2$CO$_3$ (0.56 g, 4 mmol) in dry acetonitrile (350 mL) were stirred at room temperature under an argon atmosphere for 72 hours. At the end of this period the colorless mixture was filtered and the solvent was removed from the filtrate in a rotary evaporator. The yellow oily product obtained was dried in vacuo. Yield: 0.38 g, (70.63%), IR (NaCl disk), (cm^{-1}): 3290 (NH), 3061 (ArC-H), 2958–2877 (C-H),1661 (C=O),1101 (O-CH$_2$). ^{1}H-NMR (CDCl$_3$), (δ:ppm): 9.65 (s, 2H, NH), 7.92 (d, 2H, ArH), 7.65 (d, 2H, ArH), 7.42 (t, 2H, ArH), 7.20 (t, 2H, ArH), 3.68 (s, 4H, O=CCH$_2$Cl) 3.43(t, 8H, OCH$_2$), 2.81 (t, 8H, SCH$_2$), ^{13}C-NMR (CDCl$_3$), (δ:ppm): 167.63, 137.83, 136.57, 132.43, 131.06, 128.59, 127.21, 69.28, 68.70, 42.15, 38.18, 36.14, 32.28, Anal. Calc. for $C_{24}H_{30}N_2O_4S_4$: C, 53.51, H, 5.57, N, 5.20. Found: C, 53.23, H, 5.13, N, 5.28. MS (LC-MS/ms) (m/z): 561 $[M + Na]^+$.

Synthesis of 9,10,12,13,23,24,26,27,29,30-decahydro-5H,15H-dibenzo[h,w] [1,4,7,13,16,19,25-,10,22] dioxapentathiadiazacycloheptacosine-6,16(7H,17H)-dione (11)

A mixture of (7) (0.517 g, 1 mmol), 2-mercaptoethylsulfide (0.154 g, 1 mmol), and K$_2$CO$_3$ (0.56 g, 4 mmol) in dry acetonitrile (350 mL) was stirred at room temperature under an argon atmosphere for 72 hours. At the end of this period the colorless mixture was filtered. The solvent was removed from the filtrate under reduced vacuum in a rotary evaporator. The white solid obtained was dried in vacuo. It was recrystallized from ethanol (yield: 0.32 g, 81%; mp 148–150°C, IR (KBr tablet), (cm^{-1}): 3262(NH), 3061 (ArC-H), 2918–2867 (C-H), 1676 (C=O), 1103 (O-CH$_2$). ^{1}H-NMR (CDCl$_3$), (δ:ppm): 9.93 (s, 2H, NH), 8.20 (d, 2H, ArH), 7.28 (d, 2H, ArH), 7.15 (t, 2H, ArH), 7.05 (t, 2H, ArH), 4.38(s, 4H, O=CCH$_2$Cl) 3.58 (t, 8H, OCH$_2$), 2.95 (t, 12H, SCH$_2$). ^{13}C-NMR (CDCl$_3$), (δ:ppm): 167.64, 139.40, 135.50, 129.89, 124.53, 122.99, 120.20, 70.20, 69.51, 37.61, 35.96, 33.43. Anal. Calc. for $C_{26}H_{34}N_2O_4S_5$: C, 52.17, H, 5.68, N, 4.68, Found: C, 51.83, H, 5.64, N, 4.82. MS (LC-MS/ms) (m/z):598 $[M + 1]^+$.

Solvent Extraction

Extraction experiments were performed according to the published procedure (15). Metal picrates were prepared by the stepwise addition of a 1×10^{-2} M solution of metal nitrate solution to a 1.25×10^{-5} M aqueous picric acid solution and then shaking the mixture at 25°C for 1 h.

An organic solution containing 1.25×10^{-4} M ligand and an aqueous solution containing metal picrate (1.25×10^{-5} M) were placed in a stoppered flask, and shaken for 1 h at 25 ± 0.1°C. The resulting mixture was allowed to stand for at least 2 h at that temperature in order for the complete phase separation to occur. 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. Determination of the extractability was based on the absorbance of picrate ion in the aqueous solutions. The extractability was calculated from Eq. (1).

$$E\ (\%) = [(A_0 - A)/A_0] \times 100, \tag{1}$$

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 against the ligand concentration was examined. The concentration range of the ligand was from 2.5×10^{-6} to 1.25×10^{-4} M.

For the present systems, the general extraction equilibrium is assumed to be given by Eq. (2).

$$M^{n+}_{aq} + nPic^{-}_{aq} + mL_{org} \rightleftharpoons [M(Pic)_n(L)_m]_{org} \tag{2}$$

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 (16).

$$\mathrm{Log}\{D/[Pic^{-}]^{n}\} = \log K_{ex} + m \log[L] \tag{3}$$

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

RESULTS AND DISCUSSION

The preparation of the new compounds containing nitrogen, oxygen and sulfur donor atoms, (3), (5), (7), (9), and (11) is shown in Fig. 1. The structures of

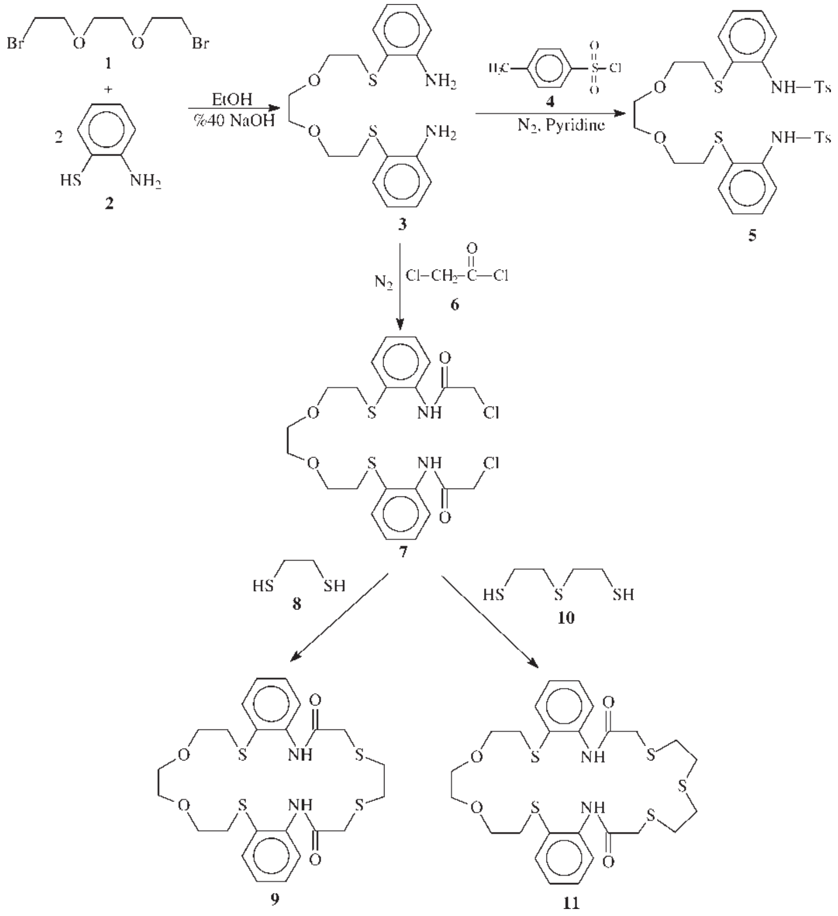

Figure 1. The synthetic pathways to the crown ethers used in the present study.

these compounds were characterized by a combination of elemental analysis and IR, ^{1}H NMR, ^{13}C NMR and MS data.

2-{[2-(2-{2-[(2-Aminophenyl)thio]ethoxy}etoxy)ethyl]thio}phenylamine (3) was synthesized by the reaction of 1,9-dibromo-3,6-dioksanonan (1) (14) with 2-aminothiophenol in ethanol under an argon atmosphere in a Schlenk system. The IR spectra of compound (3), which shows the presence of aromatic NH_2 stretching vibrations at $3449-3349\ cm^{-1}$, was in accord with the proposed structure. In the ^{1}H NMR spectrum of (3), a singlet at $\delta = 3.22$ ppm for aromatic NH_2 protons was in accord with the proposed structure. The ^{13}C NMR spectrum of (3) can be taken as a clear evidence for the formation of SCH_2 groups. The corresponding peaks were observed at $\delta = 34.44$ ppm. The expected molecular ion peak for (3) was observed at $m/z = 365[M + 1]^+$.

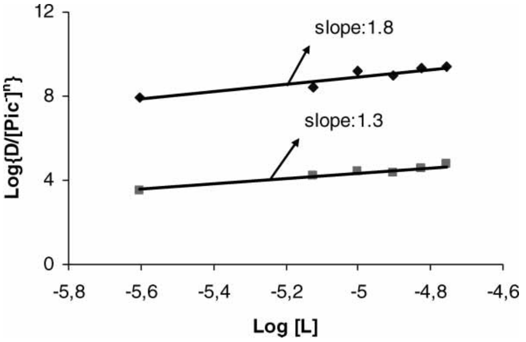

Figure 2. Log $\{D/[Pic^-]^n\}$ versus log [L] for the extraction of metal-picrate to dichloroethane phase with ligand (9). (■): Ag^+ and (◆): Hg^{2+}.

Compound (5) was obtained by the reaction of compound (3) with toluene-p-sulfonyl (4). In the IR spectrum of compound (5), the NH stretching vibration was observed at 3248 cm^{-1}. In the ^1H NMR, spectrum of compound (5), the disappearance of singlet at $\delta = 3.22$ belonging to aromatic NH_2 protons for compound (3) and appearance of the chemical shifts belonging to NH, Tos-Ar-H protons at $\delta = 8.18$ and 7.48 ppm, respectively. These values are in accord with the proposed structure. ^{13}C NMR spectral data are also in good agreement with this structure. The expected molecular ion peak for (5) was observed at $m/z = 695$ $[M + Na]^+$.

N-(2-{[2-(2-{2-[(2-aminophenyl)thio]ethoxy}ethoxy)ehyll]thio}phenyl)-2-chloroacetami de (7) was obtained by the reaction of compound (3) with chloroacetylchloride (6). IR spectrum of compound (7), the disappearance of aromatic NH_2 stretching vibrations of compound (3) after introduction of amide function, and presence of NH, C=O group stretching vibrations at 3280 and 1665 cm^{-1}, respectively, are in accord with the proposed structure. In the ^1H NMR, spectrum of compound (7), the disappearance of singlet at $\delta = 3.22$ belonging to NH_2 protons for compound (3) and appearance of the chemical shifts corresponding to amide NH protons were observed at $\delta = 9.20$ as a singlet. The C=O group of compound (7) gave a carbon resonance at $\delta = 164.22$ in the ^{13}C NMR spectrum of compound (7). The expected molecular ion peak for (7) was observed at $m/z = 539$ $[M + Na]^+$ and 540 $[M + Na + 1]^+$.

The reaction of compound (7) with 1,2-ethanedithiol (8) in the presence of four-fold excess of anhydrous K_2CO_3 in acetonitrile at room temperature under an argon atmosphere afforded compound (9). The IR spectrum of compound (9) is almost identical to that of compound (7) with only small wavelength changes. The formation of the macrocyclic compound (9) was indicated by the appearance of SCH_2 protons at $\delta = 2.81$ ppm as a triplet in the ^1H NMR spectrum of (9). The ^{13}C NMR spectrum of (9) indicated a new resonance for the SCH2 carbons at $\delta = 32.28$ ppm when compared with the ^{13}C NMR spectrum of (7). The mass spectrum of (9) displayed the expected molecular ion peak at $m/z = 561$ $[M + Na]^+$.

Compound (11) was obtained by the reaction of (7) with 2-mercaptoethylsulfide (10). The IR spectrum of (11) showed NH and C=O stretching vibrations at 3262 and 1676 cm^{-1}, respectively. In the ^1H NMR spectrum of compound (11), the chemical shifts belonging to the NH and SCH_2 protons were observed at $\delta = 9.93$ and 2.95 ppm, respectively. The ^{13}C NMR spectrum of (11) indicated a new resonance for the SCH_2 carbons at $\delta = 33.43$ ppm. The mass spectrum showed a peak at $m/z = 598$ $[M + 1]^+$ indicating formation of (11).

Extraction of Metal Picrates

Table 1 shows the extractability of Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Pb^{2+}, and Co^{2+} picrates from the aqueous phase into the organic phase by compounds (5), (9), and (11). The organic solvents are dichloroethane and chloroform. It is clear that the extractability results of the ligands are different for both of the organic solvents. Compound (5) did not effectively extract all metal cations except for Hg^{2+} ion. This may depend on the soft donor atoms such as nitrogen and sulfur placed in compound (5) interaction with soft Hg^{2+} ion. It extracted Hg^{2+} ion 74.1% to chloroform phase while the extractability was below 1.0% for dichloroethane. This result shows that the extractability of Hg^{2+} ion depends on the solvent for the polyether with open ring. The high extraction of Hg^{2+} ion may result from the cooperative effect of tosyl groups with sulfur donor atoms which are on polyether chain. At the same time chloroform may show a more solvation property according to dichloroethane for resulting Hg-complex. In a previous study we showed the solvent effect on the selective extraction of Hg^{2+} with macrocyclic ligands bearing nitrogen and sulfur donor atoms (13).

Compound (9) extracted effectively Cd^{2+} and Ag^+ ions to dichloroethane phase with 95.3% and 92.1%, respectively. The extractability of Hg^{2+} was 53.8% but the other metal ions were not extracted effectively. Cd^{2+}, Ag^+, and Hg^{2+} ions are soft metal cations and affinity nitrogen and sulfur donor atoms which are located compound (9). Therefore the high extraction can be explained with hard-soft acid-base concept (5). Compound (11) extracted Ag^+, Hg^{2+}, Cd^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, and ions Co^{2+} with various E% values to the dichloroethane phase. The high value was 87.6% for Ag^+ ion. The lowest value belongs to Co^{2+} ion with 22.8%. The extraction values of Zn^{2+} and Ni^{2+} ions were below 1.0%. As seen from Table 1, the selectivity of compound (11) was not good compared with compound (9). Because compound (11) extracted almost all the metal cations except for Zn^{2+} and Ni^{2+} ions. Compound (11) has one more sulfur donor atom when compared with compound (9).

Table 1. The E% value of aqueous metal picrates for compounds (5), (9) and (11) into organic phasea

	E (%)[a,b]			E (%)[a,c]		
Metal ion	(5)	(9)	(11)	(5)	(9)	(11)
Ag^+	7.2 ± 0.2	92.1 ± 0.5	87.6 ± 0.6	2.2 ± 0.1	90.3 ± 0.7	63.1 ± 0.9
Hg^{2+}	<1.0	53.8 ± 0.8	58.5 ± 0.6	74.1 ± 0.5	82.1 ± 0.5	78.4 ± 0.5
Cd^{2+}	<1.0	95.3 ± 0.4	51.2 ± 0.7	<1.0	<1.0	<1.0
Zn^{2+}	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Cu^{2+}	3.1 ± 0.3	6.6 ± 0.2	40.5 ± 0.5	<1.0	<1.0	<1.0
Ni^{2+}	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Mn^{2+}	<1.0	<1.0	39.3 ± 0.4	1.4	<1.0	<1.0
Pb^{2+}	<1.0	<1.0	51.7 ± 0.7	<1.0	10.2 ± 0.3	<1.0
Co^{2+}	<1.0	<1.0	22.8 ± 0.6	1.9 ± 0.2	1.0 ± 0.1	2.9 ± 0.1

[a] Temperature: 25.0 ± 0.1°C; $[\text{pic}^-] = 1.25 \times 10^{-5}$ M, $[L] = 7.50 \times 10^{-5}$ M; the values and standart deviations was obtained from three independent extraction experiments. E% was calculated as percent picrate extracted into organic phase.

[b] Organic solvent:dichloroethane.

[c] Organic solvent:chloroform.

The right part of Table 1 shows the extractability results of the ligands to chloroform phase. The highest extraction value belongs to Hg^{2+} with 74.1% in the extraction to chloroform for compound (5). The other values are below 2.2%. The compound did not effectively extract all metal cations except for Hg^{2+} ion. Compound (9) extracted Cd^{2+} ion below 1.0% to chloroform phase. This result is very interesting because the same cation was extracted 95.3% to the dichloroethane phase. It is clear that the solvent is very important in the extraction of Cd^{2+} ion with the macrocycle. Compound (9) transported Ag^{+} and Hg^{2+} ions to chloroform phase with 90.3% and 82.1%, respectively. The extraction of Pb^{2+} ion was only 10.2% and the extraction of the other metal cations was below 1%. The extractability results of compound (11) are similar to compound (9). However, the latter extracted Ag^{+} and Hg^{2+} ions to the chloroform phase less effectively with 63.1% and 78.4%, respectively. Co^{2+} was extracted to the chloroform phase with 2.9%. The other results were below 2.9%. As seen from Table 1, chloroform is a more effective solvent in selective metal extraction. Especially compound (11) may be used in the selective extraction of Ag^{+} and Hg^{2+} ions from industrial waste waters.

In order to determine the composition of extracted complexes, the effect of changing ligand concentration over the distribution ratio at constant 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 Eq. (3).

Table 2 gives the relationship between the composition and the extraction constant for the ligand (9)-Ag^{+} and -Hg^{2+} cation complexes. The composition of extracted Ag-complex for compound (9) is 1:1 and its $\log K_{ex}$ value is 10.74 for dichloroethane as organic solvent. The composition of the extracted Ag-complex for compound (9) is 1:1 and its $\log K_{ex}$ value is 11.80 for chloroform as organic solvent. The compositions are the same for both solvents. But the composition of extracted Hg^{2+}-complex for the same ligand is 2:1 and its $\log K_{ex}$ value is 17.45 for dichloroethane. These results show that the 24-membered macrocycle gives the sandwich complexes with the Hg^{2+} ion. Similar experiments were made with chloroform but there was no linear

Table 2. The relationship between composition and extraction constant for the ligand (9)-metal cation complexes

	Extraction constant		Complex composition	
Metal ion	Log K_{ex}^{a}	Log K_{ex}^{b}	L:M^{a}	L:M^{b}
Ag^{+}	10.74	11.80	1:1	3:2
Hg^{2+}	17.45	–	2:1	–

[a] Organic solvent:dichloroethane.
[b] Organic solvent:chloroform.

Table 3. The relationship between composition and extraction constant for the extraction of the ligand (11)-metal cation complexes to dichloroethane phase

	Extraction constant	Complex composition
Metal ion	Log K_{ex}	L:M
Ag^+	15.10	2:1
Hg^{2+}	14.84	1:1

relationship between log $\{D/[Pic^-]^n\}$ with log [L]. Therefore we could not determine the complex composition and the log K_{ex} value for chloroform.

Table 3 shows the relationship between complex composition and extraction equilibrium constant for Ag and Hg-complexes of ligand (11) in case of dichloroethane. It is clear that the extraction equilibrium constant (log K_{ex}) is higher for Ag^+ compared to Hg^{2+} in dichloroethane. The log K_{ex} values were 15.10 and 14.84 for Ag^+ and Hg^{2+} with ligand (11), respectively. This result shows that the Ag-ligand (11) complex is extracted more efficiently to dichloroethane compared to the Hg-ligand (11) complex. This may depend on the structure of the Ag-ligand (11) complex. As seen from Table 3 the complex composition is 2:1 in this case. Namely, the ligand forms sandwich complex with Ag^+ ion. However, the same ligand forms the 1:1 complex with Hg^{2+} ion. These results show that the complex composition and the extraction constant depend on the cation properties. We obtained similar results in early studies (15).

As seen from Tables 2 and 3, the 2:1 complexes were efficiently extracted to the dichloroethane phase. This may result from good solvation of the 2:1 complex with dichloroethane. However Table 2 shows that ligand (9) forms this composition with Hg^{2+} ion and Table 3 shows that the same composition is formed with Ag^+ ion by ligand (11). Namely, the cavity size is important in complex stoichiometry. There are many examples of this concept in literature (17).

The results of the experiments at different concentrations of the ligands but at constant picrate concentration revealed the complex composition for Hg^{2+} and Ag^+ ion. Figure 2 shows, in the case of dichloroethane, the evolution of log $\{D/[Pic^-]^n\}$ when increasing the concentration of ligand (9) at constant picrate concentration. The slopes are 1.8 and 1.3 for Hg^{2+} and Ag^+ ions, respectively. In this case, the complex composition of extracted species is 2 : 1(L:M) for Hg^{2+} ion and 1:1 (L:M) for Ag^+ ion.

Figure 3 shows, in the case of chloroform, the evolution of log $\{D/[Pic^-]^n\}$ when increasing the concentration of ligand (9) at constant Ag- picrate concentration. The slope is 1.3 in this case. This result is similar to those of dichloroethane in Table 2. Consequently, ligand (9) forms the 1:1 complex with Ag^+ ion for both solvents. This result shows that the cavity of the ligand (9) fits in ionic diameter of Ag^+ ion.

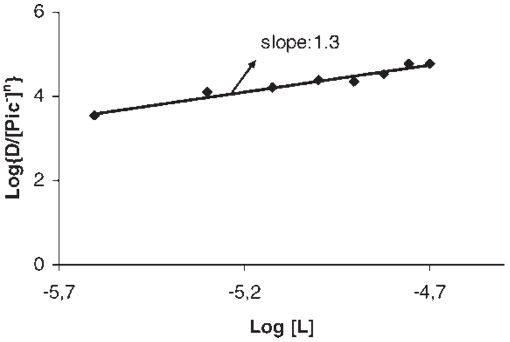

Figure 3. Log {D/[Pic$^-$]^n} versus log [L] for the extraction of Ag-picrate to chloroform phase with ligand (9).

Figure 4 shows, in the case of dichloroethane, the evolution of log {D/[Pic$^-$]^n} when increasing the concentration of ligand (11) at constant picrate concentration for Hg^{2+} and Ag^+ ion. The slopes are 1.9 and 1.2 for Ag^+ and Hg^{2+} ions, respectively. The complex composition of extracted species is 2:1 (L:M) for Ag^+ ion and 1:1 (L:M) for Hg^{2+} ion. These results are not in agreement with those of ligand. (9) As seen from Tables 2 and 3, the complex compositions of these cations for ligand (11) are exactly reverse with those of ligand (9) for dichloroethane. The ligand with larger cavity (11) forms a sandwich complex with Ag^+ ion. This result shows that the cavitiy of the ligand (11) does not fit in order to form 1:1 complex with Ag^+ ion. It prefers the 2:1 (L:M) complex composition for Ag^+ ion.

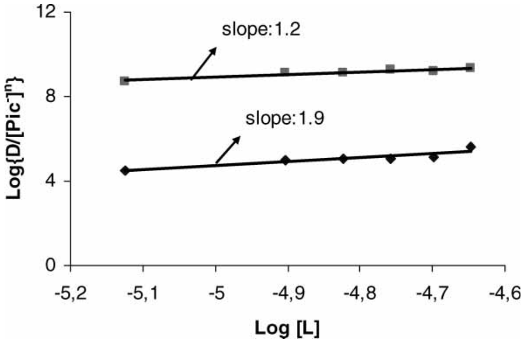

Figure 4. Log {D/[Pic$^-$]^n} versus log [L] for the extraction of metal-picrate to dichloroethane phase with ligand (11). (■): Hg^{2+} and (◆): Ag^+. Organic solvent: Dichloroethane.

CONCLUSION

It was found that the $N_2S_4O_2$ (9) and $N_2S_5O_2$ (11)-donor macrocycles extract Ag^+ and Hg^{2+} ions to the dichloroethane and chloroform phases effectively. Especially, the macrocycle with $N_2S_4O_2$ donor set, (9), extracts Cd^{2+} ion to dichloroethane phase with 95.3%. However, chloroform is a more effective solvent in the selective extraction of Ag^+ and Hg^{2+} ions for both ligands.

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