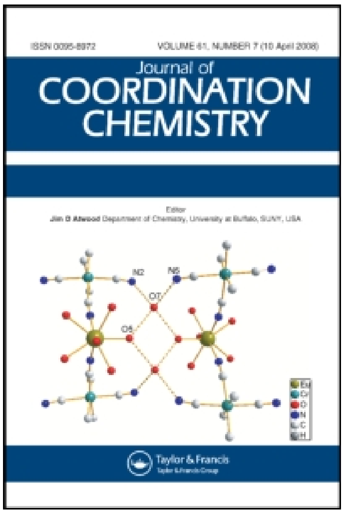

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New heavy metal ion-selective macrocyclic ligands with mixed-donor atoms and their extractant properties

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Synthetic procedures for new macrocyclic diamides with $N_2S_4O_3$- and $N_2S_5O_3$-donors were given. The corresponding macrocyclic ligands were prepared by reaction of $NaBH_4$ with the macrocyclic diamides in the presence of boron triflouride ethyl etherate in dry tetrahydrofuran. The solvent extraction method was used to evaluate metal-ion binding properties of the new ligands. The values of the extraction constants ($\log K_{ex}$) and the complex compositions were determined for the extracted complexes. The solvent extraction experiments suggested that the reduced $N_2S_5O_3$-donor macrocycle has Ag^+ selectivity compared to Pb^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+} for chloroform as organic solvent.

Keywords: Extraction constant; Mixed-donors; Macrocyclic ligand; Extractability; Selective extraction

1. Introduction

Macrocyclic multidentate ligands with an appropriate combination of ring size, identity and placement of donors exhibit a good extraction selectivity for the desired metal ions [1]. These compounds have been used for 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 [2, 3].

Since crown ethers were first recognized by Pedersen as having selective metal-ion binding properties [4, 5], various crown ethers have been prepared and their complexation behaviors are studied extensively. Coordination chemistry of mixed nitrogen, oxygen, and sulfur donor macrocycles has also been an area of increasing interest over the past 15 years. These ligands are of interest as they offer coordination of both hard donor N-ligands and soft donor, and potential p-acceptor S-ligands [6, 7].

The selectivity of alkali and alkaline earth metal ion extraction with macrocycles containing oxygen donors, primarily crown ethers, is correlated with its radius [8]. In metal extraction with macrocycles containing nitrogen–sulfur–oxygen donors, many

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factors exert influence on the extraction process, any of which may become crucial. The number of heteroatoms and their donor abilities may be decisive or the rigidity of the macrocyclic structure may be of primary importance. There are many examples of selective metal extraction with crown ethers having sulfur and nitrogen donors [9–12].

In previous studies, we have investigated the solvent extraction properties of some macrocyclic ionophores containing mixed donors for heavy metals [13, 14]. In this study, we present solvent extraction properties of one of a series of macrocyclic ligands with N, S, and O mixed donors for Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, and Ag^{+}.

2. Experimental

2,3-Dibenzo-7,10,13-trioxa-4,16-dithia-1,19-diazanonadecane (**1**) was synthesized in our laboratory according to the procedure described previously [15]. $NaBH_4$, boron trifluoride ethyl etherate, tetrahydrofuran (THF), chloroacetyl chloride (2), dichloromethane, chloroform, picric acid, $Pb(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Mn(NO_3)_2, \cdot 4H_2O$, and $AgNO_3$ were the analytical grade reagents purchased from Merck. 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.

IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer using KBr pellets or NaCl disc. ^{1}H- and ^{13}C-NMR (nuclear magnetic resonance, NMR) spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$ or DMSO, and chemical shifts are reported (δ) relative to Me_4Si as internal standard. Mass spectra (MS) were measured on a Micromass Quattro LC/ULTIMA LC-MS/MS spectrometer. Elemental analyses were determined by a LECO Elemental Analyser (CHNS O932). Melting points were measured on an electrothermal apparatus and are uncorrected. The spectrophotometric measurements were carried out with a Unicam uv2 UV-Vis spectrophotometer. In solvent extraction experiments Grant SS 30-type shaker with thermostat was used.

2.1. *Preparation of N,N′-[oxybis(ethane-2,1-diyloxyethane-2,1-diylthio-2, 1-phenylene)]bis(2-chloroacetamide) (3)*

A solution of **1** (3.1 g, 7.59 mmol) in dry benzene (38 mL) and anhydrous Na_2CO_3 (2.41 g, 22.77 mmol) under argon was prepared and the mixture was placed in an ice bath. A solution of **2** (1.72 g, 15.18 mmol) in dry benzene (76 mL) was added dropwise for approximately 2 h where the temperature of the solution was kept at 0–5°C and continually stirred at room temperature overnight. Then the mixture was filtered and the solvent was evaporated under reduced pressure to get a cream-like oily product. The crude product was crystallized from methanol. Yield: 1.12 g (26%), m.p.: 73–75°C. Anal. Calcd for $C_{24}H_{30}N_2O_5S_2Cl_2$: C, 51.33; H, 5.3; and N, 4.99. Found: C, 51.15; H, 4.28; N, and 6.21. IR (KBr pellets, cm^{-1}): 3288 (N–H), 3057 (Ar–H), 2889–2923 (C–H), 1671 (C=O), 1220–1109 ($O–CH_2$). ^{1}H-NMR ($CDCl_3$): δ 9.73 (s, 2H, NH–C=O), 8.41 (d, 2H, Ar–H), 7.58 (t, 2H, Ar–H), 7.34 (d, 2H, Ar–H), 7.12 (t, 2H, Ar–H), 4.45

(s, 4H, CH_2–Cl), 3.53 (t, 12H, O–CH_2), and 3.21 (t, 4H, S–CH_2). ^{13}C-NMR ($CDCl_3$): 164.09 (O=C–CH_2), 140.07 (Ar–C), 135.90 (Ar–C), 130.07 (Ar–C), 124.89 (Ar–C), 120.00 (Ar–C), 112.8 (Ar–C), 70.54–69.39 (O–CH_2), 43.42 (N–CH_2), and 35.55 (S–CH_2). (FAB) MS $m/z = 561$ $[M]^+$.

2.2. *Preparation of 6,7,8,9,10,12,13,15,16,26,27-decahydro-22H,29H-dibenzo[k,w][1,4,7,10-16,19,25,13,22]trioxatetrathiadiazacycloheptacosine-23,30(24H,31H)-dione (5)*

A solution of **3** (0.2 g, 0.356 mmol), dry K_2CO_3 (0.197 g, 1.42 mmol) and 1,2-etandithiol (**4**) (0.033 g, 0.356 mmol) in dry acetonitrile (50 mL) was stirred under argon at room temperature for 72 h. At the end of this period, the mixture was filtered and the filtrate was evaporated under reduced pressure to get light yellow oily product. Yield: 0.18 g (84%). Anal. Calcd for $C_{26}H_{34}N_2O_5S_4$: C, 53.60; H, 5.84; and N, 4.81. Found: C, 53.02; H, 5.28; N, 5.03. IR (NaCl disc, cm^{-1}): 3303 (N–H), 3058 (Ar–H), 2921–2862 (C–H), 1690 (C=O), 1201–1112 (OCH_2). ^{1}H-NMR ($CDCl_3$): δ 9.75 (s, 4H, NH), 8.37(d, 2H, Ar–H), 7.55 (m, 4H, Ar–H), 7.36 (d, 2H, Ar–H), 3.72 (s, 4H, O=C–CH_2), 3.54 (t, 8H, O–CH_2), 3.11 (t, 4H, S–CH_2), 2.95 (s, 8H, S–CH_2). ^{13}C-NMR ($CDCl_3$) δ: 168.55 (C=O), 138.64 (Ar–C), 133.14 (Ar–CH), 128.51 (Ar–C), 126.14 (Ar–C), 124.30 (Ar–C), 123.79.12 (Ar–C), 71.03 (O–CH_2), 41.45 (N–CH_2), and 34.76 (S–CH_2). (EI) MS $m/z = 583$ $[M + 1]^+$.

2.3. *Preparation of 6,7,9,10,12,13,15,16,23,24,26,27,30,31-tetradecahydro-22H, 29H-dibenzo-[k,w][1,4,7,10,16,19,25,13,22]trioxatetrathiadiazacycloheptacosine (6)*

A solution of **5** (0.15 g, 0.258 mmol) in dry THF (9 mL) was stirred at room temperature under argon until it dissolves and the mixture was placed in an ice bath. $NaBH_4$ (0.088 g, 2.322 mmol) was added to the mixture being stirred at 0–5°C under argon. Boron trifluoride ethyl etherate (0.40 g, 2.84 mmol) was added dropwise for approximately 3 h where the temperature was kept constant overnight. At the end of this period, one or two drop(s) of water was added to the solution and the release of H_2 gas was seen and then the solution was neutralized using aqueous NaOH (20%) until the pH value of the mixture becomes 8–9. THF was evaporated under reduced pressure and the residue was extracted with 50 mL of chloroform. The extract was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure to obtain the oily product. Yield 0.08 g (57%). Anal. Calcd for $C_{26}H_{38}N_2O_3S_4$: C, 56.31; H, 6.85; and N, 5.05. Found: C, 55.87; H, 6.38; and N, 5.42. IR (NaCl disc, cm^{-1}): 3358 (N–H), 3061 (Ar–H), 2922–2856 (C–H), 3061, and 1282–1193 (C–O). ^{1}H-NMR ($CDCl_3$): δ 7.76 (d, 2H, Ar–H), 7.46 (t, 2H, Ar–H), 6.92 (m, 4H, Ar–H), 5.71 (s, 2H, NH), 3.53 (t, 12H, O–CH_2), 2.98 (t, 4H, N–CH_2), and 2.94 (t, 12H, S–CH_2). ^{13}C-NMR ($CDCl_3$): δ 148.29 (Ar–C), 135.85 (Ar–C), 131.55 (Ar–CH), 130.02 (Ar–C), 116.27 (Ar–C), 116.18 (Ar–C), 69.68–68.83 (O–CH_2), 42.09 (N–CH_2), and 34.85 (S–CH_2). (FAB) MS $m/z = 555$ $[M + 1]^+$.

2.4. *Preparation of 6,7,8,9,10,12,13,15,16,26,27-decahydro-22H,29H-dibenzo[k,w][1,4,7,10-16,19,25,13,22]trioxapentathiadiazacycloheptacosine-23,30(24H,31H)-dione (8)*

A solution of **3** (0.8 g, 1.426 mmol), dry K_2CO_3 (0.786 g, 5.70 mmol), and mercaptoethylsulfide (**7**) (0.20 g, 1.426 mmol) in dry acetonitrile (54 mL) was stirred under argon at room temperature for 72 h. At the end of this period, the mixture was filtered and the filtrate was evaporated under reduced pressure to get light yellow product. Yield: 0.55 g (60%). Anal. Calcd for $C_{28}H_{38}N_2S_5O_5$: C, 52.34; H, 5.91; and N, 4.36. Found: C, 52.79; H, 5.98; and N, 3.99. IR (NaCl disc, cm^{-1}): 3307 (N–H), 3049 (Ar–H), 2920–2862 (C–H), 1682 (C=O), and 1240–1111 (OCH_2). ^{1}H-NMR ($CDCl_3$): δ 8.36 (s, 2H, NH), 7.93 (d, 2H, Ar–H), 7.52 (t, 2H, Ar–H), 6.80 (m, 4H, Ar–H), 3.82 (s, 4H, O=C–CH_2), 3.78 (t, 12H, O–CH_2), and 2.38 (m, 12H, S–CH_2). (FAB) MS $m/z = 681$ $[M + K]^+$.

2.5. *Preparation of 6,7,9,10,12,13,15,16,23,24,26,27,30,31-tetradecahydro-22H,29H-dibenzo-[k,w][1,4,7,10,16,19,25,13,22]trioxapentathiadiazacycloheptacosine (9)*

A solution of **8** (0.520 g, 0.809 mmol) in dry THF (110 mL) was stirred at room temperature under argon until it dissolves and the mixture was placed in an ice bath. $NaBH_4$ (0.277 g, 7.281 mmol) was added to the mixture being stirred at 0–5°C under argon. Boron trifluoride ethyl etherate (1.26 g, 8.94 mmol) was added dropwise through a dropping funnel for approximately 3 h where the temperature was kept constant overnight. At the end of this period, one or two drop(s) of water was added to the solution and H_2 gas was evolved and then the solution was neutralized using aqueous NaOH (20%) until the pH value of the mixture is in the range 8–9. THF was evaporated under reduced pressure and the residue was extracted with 50 mL of chloroform. The extract was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure to get the oily product. Yield 0.43 g (88%). Anal. Calcd for $C_{28}H_{42}N_2S_5O_3$: C, 54.72; H, 6.84; and N, 4.56. Found: C, 54.98; H, 6.52; and N, 4.18. IR (NaCl disc, cm^{-1}): 3360 (N–H), 3064 (Ar–H), 2955–2854 (C–H), and 1279–1199 (CH_2–O). ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.63 (d, 2H, Ar–H), 7.46 (t, 2H, Ar–H), 6.93 (m, 4H, Ar–H), 5.42 (s, 2H, NH), 3.55 (t, 12H, O–CH_2), 3.11 (t, 4H, N–CH_2), and 2.88 (s, 16H, S–CH_2). ^{13}C-NMR ($CDCl_3$): δ 148.59 (Ar–C), 136.72 (Ar–C), 130.34 (Ar–CH), 117.12 (Ar–C), 117.01 (Ar–C), 110.04 (Ar–C), 70.55–69.83 (O–CH_2), 42.81 (N–CH_2), and 35.56 (S–CH_2). (FAB) MS $m/z = 615$ [M + 1].

2.6. *Extraction method*

The previous method was used in the extraction experiment [16]. An organic solution (10 mL) of ligand (7.5×10^{-5} mol L^{-1}) and an aqueous solution (10 mL) containing 1.25×10^{-5} mol L^{-1}picric acid and 1×10^{-2} mol L^{-1} metal nitrate were placed in a stoppered flask and shaken for 2 h at 25.0 ± 0.1°C. This period of shaking was enough to establish equilibrium between the two phases. Dichloromethane and chloroform were used as organic solvents. 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 ($E\%$) was determined based on absorbance of picrate in aqueous solutions. The extractability was calculated from the following equation:

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

where A_0 is the absorbance in the absence of ligand and A 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 ligand concentration was examined. The range of the ligand concentration was $2.5 \times 10^{-6} - 7.50 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$.

The general extraction equilibrium is assumed to be given by the following equation.

$$\mathrm{M}^{n+}_{\mathrm{aq}} + n\,\mathrm{Pic}^- + m\,\mathrm{L}_{\mathrm{org}} \leftrightarrow [\mathrm{M(Pic)}_n(\mathrm{L})_m]_{\mathrm{org}}, \tag{2}$$

where "aq" denotes aqueous solution and "org" organic solution. The following logarithmic expression is valid for the above extraction system.

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

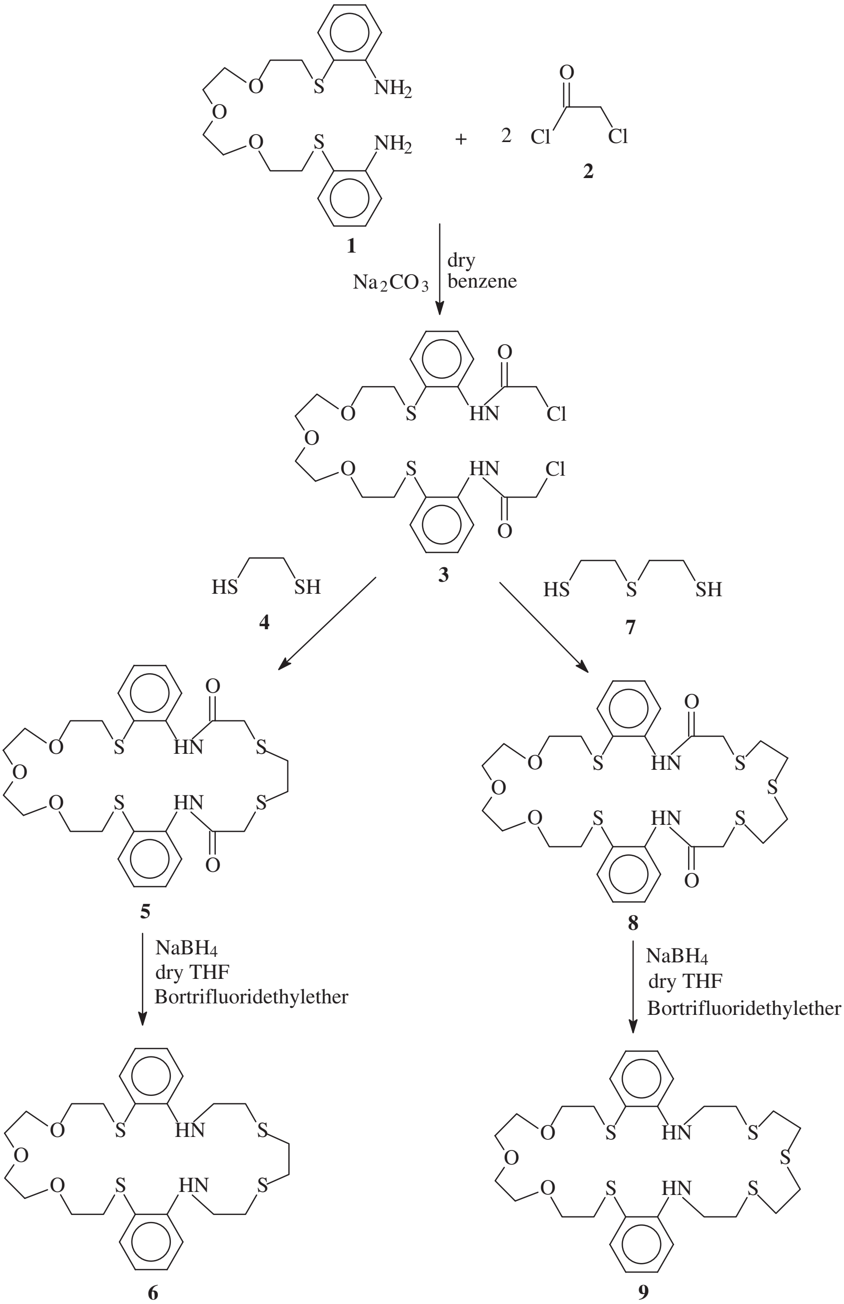
The plot of log $\{\mathrm{D}/[\mathrm{Pic}^-]^n\}$ as a function of log [L] should give a straight line with a slope of m and log K_{ex} can be calculated from the intercept by using equation (3).

3. Results and discussion

The preparations of four macrocyclic ligands containing nitrogen, sulfur, and oxygen donors **5**, **6**, **8**, and **9** are shown in scheme 1. The new ligands were characterized by a combination of elemental analysis, IR, ^{1}H-NMR, ^{13}C-NMR, and MS spectral data.

Reaction of **1** with chloroacetylchloride in dichloromethane at 0–5°C under argon afforded *N*,*N′*-[oxybis(ethane-2,1-diyloxyethane-2,1-diylthio-2,1-phenylene)]-bis(2-chloroacetamide) (**3**) in a Schlenk system in 26% yield. In the IR spectrum of **3**, the disappearance of aromatic primary–NH_2 vibrations of **1** after introduction of amide function, and presence of –NH, C=O group stretching vibrations at 3288 and 1671 $\mathrm{cm^{-1}}$, respectively, confirmed the proposed structure. In the ^{1}H-NMR spectrum of **3**, the singlet at $\delta = 4.45$ ppm corresponded to methylene protons between C=O and Cl groups. The protons of –NH were observed at $\delta = 9.73$ ppm as a singlet. The C=O of **3** gave a carbon resonance at $\delta = 164.09$ ppm in the ^{13}C-NMR spectrum. The MS of **3** displayed the expected molecular ion peak at $m/z = 561$ $[\mathrm{M}]^+$ in the MS obtained using the (EI) MS technique.

The reaction of **3** with ethane-1,2-dithiol and 4-fold excess of anhydrous K_2CO_3 in dry acetonitrile at room temperature under argon afforded 6,7,8,9,10,12,13,15,16,26,27-decahydro-22H,29H-dibenzo[k,w][1,4,7,10–16,19,25,13,22]-trioxatetrathiadiazacycloheptacosine-23,30(24H,31H)-dione (**5**) in 84% yield. The IR spectrum of **5** is almost identical to that of **3** with small changes in wave numbers. The formation of macrocycle was confirmed by the appearance of a new resonance for S–CH_2



Scheme 1. Synthetic pathways to the new macrocyclic ligands used in this study.

at $\delta = 2.95$ ppm in the ^{1}H-NMR spectrum. The ^{13}C-NMR spectrum of **5** indicated new resonance for S–CH_2 carbons at $\delta = 34.76$ ppm when compared with the ^{13}C-NMR spectrum of **3**. The MS of **5** displayed the expected molecular ion peak at $m/z = 583$ $[M + 1]^+$.

The reduced macrocycle 6,7,9,10,12,13,15,16,23,24,26,27,30,31-tetradecahydro-22H,29H-dibenzo[k,w][1,4,7,10,16,19,25,13,22]trioxatetrathiadiazacycloheptacosine (**6**) was obtained (57% yield) from **5** by using sodium borohydride–boron trifluoride ethyl etherate in dry THF at 0–5°C under argon. Analytical and spectroscopic data of **6** clearly confirmed the reduction reaction. In the IR spectrum of **6**, the stretching vibrations belonging to C=O in **5** were absent after reduction. Disappearance of the singlets at $\delta = 3.72$ ppm in the α-bisamide macrocyclic **6** and appearance of a singlet at $\delta = 5.71$ ppm for –NH and a triplet at $\delta = 2.98$ ppm for $-NCH_2$ confirmed the proposed structure. The disappearance of the C=O signals, along with the appearance of a new peak at $\delta = 42.09$ ppm for $N-CH_2$ in the ^{13}C-NMR spectrum of **6** can be taken as clear evidence for the formation of reduced macrocycle. The expected molecular ion peak for **6** was observed at $m/z = 555$ $[M + 1]^+$.

The reaction of **3** with 2,2′-dithioethanethiol and 4.5-fold excess of anhydrous K_2CO_3 in dry acetonitrile at room temperature under argon afforded 6,7,8,9,10,12,13,15,16,26,27-decahydro-22H,29Hdibenzo[k,w][1,4,7,10,16,19,25,13,22]trioxapentathiadiazacycloheptacosine-23,30(24H,31H)-dione (**8**) in 60% yield. The IR spectrum of **8** is almost identical to that of **3** with small changes in wave numbers. The formation of macrocycle was confirmed by appearance of a new resonance for $S-CH_2$ at $\delta = 2.38$ ppm as multiplet in the ^1H-NMR spectrum of **8** in $CDCl_3$. The MS of **8** displayed the expected molecular ion peak at $m/z = 681$ $[M + K]^+$.

The reduced macrocycle 6,7,9,10,12,13,15,16,23,24,26,27,30,31-tetradecahydro-22H,29H-dibenzo[k,w][1,4,7,10,16,19,25,13,22]trioxapentathiadiazacycloheptacosine (**9**) was obtained from **8** by using sodium borohydride–boron trifluoride ethyl etherate in dry THF at 0–5°C under argon in 88% yield. Analytical and spectroscopic data of **9** clearly confirmed the success of the reduction. In the IR spectrum of **9**, the stretching vibrations belonging to C=O group at 1682 cm^{-1} in **8** were absent after reduction. The disappearance of the singlets at $\delta = 8.36$ ppm in **8** and appearance of a singlet at $\delta = 5.42$ ppm for –NH and a triplet at $\delta = 3.11$ ppm for $-NCH_2$ confirmed the proposed structure. The disappearance of the C=O signals, along with appearance of a new peak at $\delta = 42.81$ ppm for NCH_2 in the ^{13}C-NMR spectrum of **9** can be taken as a clear evidence for formation of reduced macrocycle. The expected molecular ion peak for **9** was observed at $m/z = 615$ $[M + 1]^+$.

3.1. *Extraction of metal picrates*

Ni^{2+}, Mn^{2+}, Co^{2+}, Ag^+, Cd^{2+}, and Pb^{2+} picrates were used in extraction studies. The experiments were carried out at 25 ± 0.1°C with the solution of the ligands in chloroform and dichloromethane.

The extractability of Ni^{2+}, Mn^{2+}, Co^{2+}, Ag^+, Cd^{2+}, and Pb^{2+} picrates from the aqueous phase into the chloroform phase by ligands is given in table 1. Ligand **3** extracts only Ag^+ effectively with 66.3%. Co^{2+} is extracted below 2.0% in this case. This result shows that the polyether with an open ring, **3**, shows important selectivity for Ag^+. Similar results were obtained for Hg^{2+} picrate with the similar diamide compound without the oxyethylene moiety [16]. In the previous study, the extractability was found only for Ag^+ at 5.2% with the diamide compound containing only sulfur donors [16]. However, the introduction of three oxygen donors into the structure causes

Table 1. The extractability of aqueous metal picrates for **3**, **5**, **6**, **8**, and **9** into the chloroform phase.[a]

	Extractability (%)				
Metal ion	**3**	**5**	**6**	**8**	**9**
Ni^{2+}	<1.0	<1.0	5.0 ± 0.3	2.0 ± 0.1	<1.0
Mn^{2+}	<1.0	3.5 ± 0.1	1.5 ± 0.1	5.4 ± 0.2	<1.0
Co^{2+}	1.2 ± 0.9	<1.0	<1.0	<1.0	<1.0
Ag^{+}	66.3 ± 0.5	<1.0	87.4 ± 0.7	82.4 ± 0.2	87.1 ± 0.9
Cd^{2+}	<1.0	<1.0	9.7 ± 0.9	<1.0	<1.0
Pb^{2+}	<1.0	<1.0	22.8 ± 0.5	<1.0	<1.0

[a] Temperature: 25.0 ± 0.1°C; aqueous phase (10 mL); $[pic^-] = 1.25 \times 10^{-5}\,mol\,L^{-1}$, organic phase (10 mL); $[L] = 7.50 \times 10^{-5}\,mol\,L^{-1}$; the values and SDs calculated from three independent extraction experiments.

Table 2. The extractability of aqueous metal picrates for **3**, **5**, **6**, **8,** and **9** into the dichloromethane phase.[a]

	Extractability (%)				
Metal ion	**3**	**5**	**6**	**8**	**9**
Ni^{2+}	4.3 ± 0.1	<1.0	62.0 ± 0.2	37.2 ± 0.1	<1.0
Mn^{2+}	13.7 ± 0.2	<1.0	43.6 ± 0.1	10.6 ± 0.3	<1.0
Co^{2+}	5.2 ± 0.4	<1.0	<1.0	4.5 ± 0.1	83.4 ± 0.5
Ag^{+}	80.4 ± 0.5	10.0 ± 0.1	87.2 ± 0.6	93.2 ± 0.8	92.1 ± 0.5
Cd^{2+}	<1.0	<1.0	3.5 ± 0.6	33.1 ± 0.2	<1.0
Pb^{2+}	4.1 ± 0.1	<1.0	49.1 ± 0.4	10.2 ± 0.1	10.5 ± 0.2

[a] Temperature: 25.0 ± 0.1°C; aqueous phase (10 mL); $[pic^-] = 1.25 \times 10^{-5}\,mol\,L^{-1}$, organic phase (10 mL); $[L] = 7.50 \times 10^{-5}\,mol\,L^{-1}$; the values and SDs calculated from three independent extraction experiments.

an increment in the extractability of Ag^+ with 66.3%. Ligand **5** did not effectively extract all metal cations; the extractability was only 3.5% for Mn^{2+}.

It is clear that **6**, which is the reduced form of **5**, extracted all the tested metal cations to chloroform except for Co^{2+}. This result shows that the reduced form in the extraction with chloroform is less selective for Ag^+ with the macrocyclic diamide. As seen from table 1, the extractability of Ag^+ (87.4%) increased compared to that of the corresponding diamide **5**. Ligand **8** has only one more sulfur donor than **5**. However, this increase in the number of sulfurs causes a pronounced effect in the extraction efficiency of Ag^+ picrate. Ag^+ was extracted by 82.4% to the chloroform phase with **8**, while the extraction efficiency was below 1.0% with **5**. This indicates the importance of the number of donors in the macrocycle during the transport of Ag^+. Another interesting result seen from table 1 is the selective extraction of Ag^+ picrate with **9**. Ligand **9** is the reduced form of **8** and shows better selectivity for Ag^+ with respect to **6**, which has one less sulfur donor. Therefore, the results confirm that the number and the kind of donors and their location in the cavity of the macrocyclic ligand are very important in selective extraction. These are in agreement with the results for crown ether ligands with mixed donors [8].

As seen from table 2, which shows the extractability results of the ligands to the dichloromethane phase, **3** extracted all metal cations except Cd^{2+}, showing that dichloromethane causes less selectivity in the extraction of the tested metal cation than chloroform. When tables 1 and 2 are compared, it can be seen that dichloromethane is

Table 3. The relationship between the composition and extraction constants for the complexes of **6** and **9**.

Metal ion	Ligand **6**				Ligand **9**	
	$(L:M)^a$	$(\log K_{ex})^a$	$(L:M)^b$	$(\log K_{ex})^b$	$(L:M)^a$	$(\log K_{ex})^a$
Ag^+	3 : 1	20.29	3 : 1	17.54	3 : 1	19.74
Pb^{2+}	1 : 1	14.22	–	–	–	–

[a] Dichloromethane.
[b] Chloroform.

more effective in the extraction of Ag^+ picrate with respect to chloroform with **5** with 10.0% to the dichloromethane phase and **6** extracted all the metal cations to the dichloromethane phase except Co^{2+}. The extractability of Ni^{2+}, Mn^{2+}, and Pb^{2+} increased for dichloromethane with respect to chloroform with **6**, showing that solvent is important in the extraction efficiency. The values of extractability (%) in dichloromethane increased to 62.0 and 43.6 for Ni^{2+}, and Mn^{2+}, respectively. We found an increment in the extraction of Ni^{2+}, Mn^{2+}, and Co^{2+} with dichloromethane with respect to chloroform for an aromatic macrocyclic ligand bearing nitrogen–sulfur mixed donors [17]. The same effect was valid for Pb^{2+} and Cd^{2+} in the previous study [17]. In this study, we obtained similar results except for Cd^{2+} with **6**. Ligand **8** extracted all the metal cations with various extractability values (%)to dichloromethane. The highest value was 93.2% for Ag^+ and the lowest value belongs to Co^{2+} with 4.5%. When the extraction results of **5** and **8**, diamide macrocycles, are compared, **5** is more selective but not as effective for Ag^+, showing that the cavity size and the number of donors of the macrocycle with nitrogen–sulfur–oxygen mixed donors are significant in selective metal cation transport. Recently, we showed that diamide macrocyclic ligands have more selectivity than the corresponding reduced macrocycles [17, 18]. The extraction selectivity results of **5** and **6** agree with that of our previous results. However, table 2 shows opposite results for **8** and its reduced form **9**. The reduced ligand (**9**) shows better selectivity for Ag^+ with respect to that of the corresponding diamide **8** for dichloromethane. Another interesting result belongs to Co^{2+}. As seen from table 2, **9** extracted Co^{2+} to dichloromethane in 83.4%, while the same ligand extracted it to chloroform below 1.0% (table 1). It is clear that the solvent has pronounced effect in the extraction of Co^{2+} ion with **9**.

Table 3 gives the relationship between composition and extraction constants for the complexes of **6** and **9** with Pb^{2+} and Ag^+ for chloroform and dichloromethane; 3 : 1 complex composition was obtained with these macrocycles for Ag^+. However, the $\log K_{ex}$ value was higher for dichloromethane than chloroform. As seen from table 3, we could not calculate the $\log K_{ex}$ value for some cases in the extraction of Pb^{2+} because of irregular evolution between $\log \{D/[Pic^-]^n\}$ and $\log [L]$. The macrocycle (**6**) carrying $N_2O_3S_4$ donors transports Pb^{2+} to dichloromethane as a 1 : 1 complex, but the same ligand forms the 3 : 1 complex with Ag^+. The $\log K_{ex}$ values for Pb^{2+} and for Ag^+ complexes are 14.22 and 20.29, respectively. Ag^+ is extracted better than Pb^{2+} with **6** in dichloromethane. This result is also confirmed by the extractability results of this ligand in table 1. In table 3, the right-hand side shows the complex composition and extraction equilibrium constants for the Ag^+ complex of **9** in dichloromethane. It is clear that the

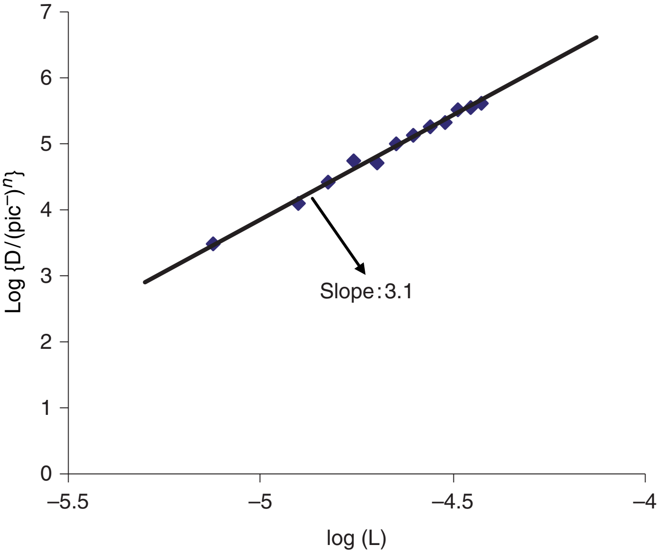


Figure 1. Log$\{D/[Pic^-]^n\}$ *vs*. log [L] for the extraction of Ag picrate to dichloromethane phase with **9**.

extraction equilibrium constant (log K_{ex}) is lower for Ag^+ than **6**. However, the complex composition is the same 3 : 1 in this case. These results suggest that the extraction constant depends on both the kind of solvent and the structure of the cation.

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] gave a straight line with a slope of m and log K_{ex} was calculated from the intercept by equation (3). Figure 1 shows, in the case of dichloromethane, the evolution of log $\{D/[Pic^-]^n\}$ while increasing the concentration of **9** at constant picrate concentration and the slope is calculated as 3.1, showing that the complex composition of extracted species is 3 : 1(L : M) for Ag^+.

Complex compositions were also confirmed with the molar ratio method. For this, the extractability (%) of the ligands was plotted against the ratio of [ligand]/[metal]. Figure 2 shows the molar ratio plot for Ag^+ ion with **9**, where the organic solvent was dichloromethane and it clearly shows the formation of the 3 : 1 complex.

4. Conclusion

We have obtained two new macrocyclic diamides containing $N_2S_4O_3$- and $N_2S_5O_3$-donors. These macrocyclic ligands were prepared by reaction of $NaBH_4$ with macrocyclic diamides in the presence of boron trifluoride ethyl etherate in dry THF. The solvent extraction method was used to evaluate metal-ion binding properties of the new ligands. Table 3 gives the relationship between composition and extraction constants for the complexes of **6** and **9** with Pb^{2+} and Ag^+ for chloroform and dichloromethane. Ligand **8** extracted all the metal cations with various extractability

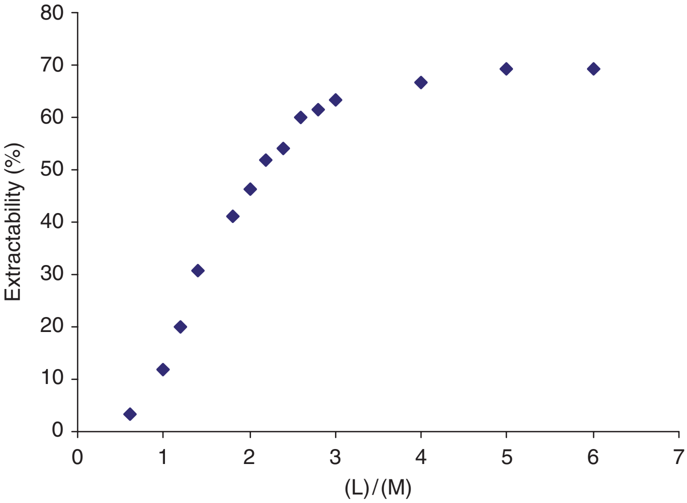


Figure 2. Dependence of extractability (%) of **9** on the concentration of Ag^+ in the extraction with dichloromethane.

values (%)to dichloromethane. The highest value was 93.2% for Ag^+, whereas the lowest value belongs to Co^{2+} with 4.5%. When the extraction results of **5** and **8**, which are diamide macrocycles, are compared, **5** is more selective but not as effective for Ag^+.

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