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Synthesis and metal ion binding properties of thiaaza crown macrocycles

Hakan Alp[b], Halil Zeki Gök[a], Halit Kantekin[a], Ümmühan Ocak[a,*]

[a] *Department of Chemistry, Faculty of Arts & Sciences, KTÜ, 61080 Trabzon, Turkey*
[b] *Department of Chemistry, Faculty of Arts & Sciences, Giresun University, 28049 Giresun, Turkey*

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ABSTRACT

Two new macrocyclic ligands (**3**) and (**4**), containing nitrogen–sulfur donor atoms, were designed and synthesized in a multi-step reaction sequence. The macrocycles (**3**) and (**4**) were used in solvent extraction of metal picrates such as Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, and Pb^{2+} from aqueous phase to the organic phase. The metal picrate extractions were investigated at $25 \pm 0.1\,^\circ C$ by using UV–visible spectrometry. The extractability and selectivity of the mentioned metal picrates were evaluated according to the organic solvents. The values of the extraction constants ($\log K_{ex}$) and the complex compositions were determined for the extracted complexes.

1. Introduction

Synthetic macrocycles have been known for over 75 years, although a real spate of publications in this area was observed in the late 1960s [1]. In that period, more than 5000 macrocyclic compounds were reported, and since then their number has increased markedly from year to year. The "hard" ether–oxygen-containing macrocycles show a binding preference toward "hard" alkali and alkaline earth metal cation, but the incorporation of "soft" sulfide or amine linkages shifts its preference toward "soft" heavy metal cations [2]. It has been demonstrated that macrocyclic ligands containing nitrogen–sulfur donor atoms can behave as highly selective complexing agents for transition metal cations [3–5]. The aza-ligands are more selective against hard ions whereas the thia-ligands preferentially bind soft ions. Selectivity can be enhanced by combining different donor atoms in one ring system. Therefore, nitrogen–sulfur macrocycles having different cycle size or arrangement have been prepared and their complexation properties have been investigated with various metal cations [6–8].

Solvent extraction is an available and convenient method for the investigation of ability of macrocyclic polyethers with various metal ions. At the same time, it can be used in treatment of wastewater containing heavy metal ions such as Hg^{2+}, Cd^{2+}, and Pb^{2+}. Especially, mercury is considered a highly dangerous element because of its toxic properties. Many mercury compounds are produced in industrial processes and disposed off to the environment.In the previous studies, we have investigated solvent extraction properties of some macrocyclic ionophores containing diazapentaoxa, diazatetrathia, and diazapentathia mixed donor atoms for heavy metals [9–11]. In this work, we have been interested in the design and synthesis of two novel macrocyclic ligands with diazatetrathia mixed donor atoms, and also 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+} have been investigated.

2. Experimental

Compound (**1**) was synthesized in our laboratory according to the procedure described previously [12]. Chloroacetylchloride was purchased from Lanchester. $NaBH_4$, boron trifluoride ethyl etherate, THF, and chloroform were obtained from Merck. Chloroform, dichloromethane, picric acid, $NaHCO_3$, $Pb(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Mn(NO_3)_2{\cdot}4H_2O$, $AgNO_3$, and $Hg(NO_3)_2{\cdot}H_2O$ were the analytical grade reagents and were purchased from Merck. Anhydrous K_2CO_3, and anhydrous Na_2CO_3 were obtained from Fluka. Ethane-1,2-dithiol was purchased from Aldrich. 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 FTIR spectrophotometer using KBr pellets or NaCl disc. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, and DMSO, and chemical shifts are reported (δ) relative to Me_4Si as an internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. Elemental

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[*] Corresponding author. Tel.: +90 462 377 25 96; fax: +90 462 325 31 96.
E-mail address: ummuhanocak@yahoo.com (Ü. Ocak).

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analysis was determined by a LECO Elemental Analyser (CHNS O932). Melting points were measured on an electrothermal apparatus.

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.

*2.1. 9,10,21,22-Tetrahydro-5H,12H,20H-dibenzo[b,n][1,7,10,16,4,13]tetrathiadiazacyclononadecyne-6,13(7H,14H)-dione (**3**)*

A solution of ethane-1,2-dithiol **2** (0.063 g, 0.677 mmol) in dry dimethylformamide (30 ml) in a dropping funnel and a solution of **1** (0.3 g, 0.677 mmol) in dry dimethylformamide (30 ml) in a dropping funnel were added simultaneously under stirring and dry inert gas to dry DMF (15 ml) containing anhydrous sodium carbonate (0.287 g, 2.7 mmol) over 1.5 h at room temperature. After addition was completed, reaction mixture was stirred at room temperature for another 2 h. The reaction was monitored by thin layer chromatography [pentane–ethyl acetate (6:4)]. At the end of this period, the mixture was filtered off and filtrate was evaporated under reduced pressure to dryness. Water (500 ml) was added to the crude product and stirred at room temperature for 1 h and then filtered off. The white precipitate was washed with ethanol and diethyl ether then dried in vacuum. Yield: 0.31 g (95%), mp 222–223 °C. IR (KBr tablet) (cm^{-1}): 3273 (–NH), 3048 (CH$_{Ar}$), 2916 (CH$_3$), 1671 (C=O), 1579, 1521, 1435, 1302, 758. ^{1}H NMR (DMSO-d_6) δ: 9.70 (s, 2H, NH), 7.72 (d, 2H, ArH, j = 6.7), 7.47 (d, 2H, ArH, j = 7.4), 7.25 (t, 2H, ArH), 7.14 (t, 2H, ArH), 3.45 (s, 4H, O=CCH$_2$S), 3.09 (t, 4H, SCH$_2$), 2.92 (m, 4H, SCH$_2$), 1.74 (m, 2H, SCH$_2$). ^{13}C NMR. (DMSO-d_6) δ: 167.97 (C=O), 137.83, 132.58, 127.88, 126.97, 125.24, 123.07 (ArC), 35.49 (O=CCH$_2$S), 33.02, 31.94 (SCH$_2$), 28.17. Anal. Calc. for $C_{21}H_{24}N_2O_2S_4$: C, 54.28; H, 5.21; N, 6.05. Found: C, 54.46; H, 4.98; N, 5.87%. MS (LC-MS/MS) m/z: 465 [M+1]$^+$.

*2.2. 6,7,9,10,13,14,21,22-Octahydro-5H,12H,20H-dibenzo[b,n][1,7,10,16,4,13]tetrathiadiaza cyclononadecyne (**4**)*

A solution of **3** (0.2 g, 0.432 mmol) in dry THF (30 ml) was heated and stirred under argon until **3** was dissolved, and the mixture was allowed to cool to room temperature and then placed in an ice salt bath. NaBH$_4$ (0.148 g, 3.87 mmol) was added to stirring mixture at 0–5 °C under argon. Boron trifluoride ethyl etherate (0.672 g, 4.74 mmol) was added dropwise through a dropping funnel to stirring mixture over a period in which the temperature of the solution was kept at 0–5 °C and then stirring was continued at room temperature overnight. The reaction was monitored by thin layer chromatography [pentane–ethyl acetate (6:4)]. At the end of this period, the mixture was filtered and filtrate was neutralized with aqueous sodium hydroxide (15%) at 0–5 °C until the pH value of the mixture was to 8–9. Tetrahydrofuran was evaporated under reduced pressure and the residue was filtered off, washed with water, ethanol and diethyl ether, and then dried in vacuum. The crude product was purified by chromatography on silica gel. The elution was carried out with chloroform. The product was obtained as yellow oil. Yield: 0.15 g (79%). IR (NaCl disk) (cm^{-1}): 3360 (–NH), 3064 (CH$_{Ar}$), 2919–2852 (CH$_3$), 1588, 1500, 1450, 1318, 1281, 1113, 1037, 747. ^{1}H NMR (CDCl$_3$) δ: 7.38 (d, 2H, ArH, j = 6.3), 7.18 (t, 2H, ArH), 6.66 (d, 2H, ArH, j = 7.1), 6.60 (t, 2H, ArH), 5.44 (s, 2H, NH), 3.38 (t, 4H, NCH$_2$), 2.91-2.81 (m, 12H, SCH$_2$), 1.61 (m, 2H, SCH$_2$). ^{13}C NMR (CDCl$_3$) δ: 148.55 136.04, 130.00, 117.91, 117.21, 110.17 (ArC), 42.59 (NCH$_2$), 34.40, 32.66, 32.29 (SCH$_2$), 29.72. Anal. Calc. for $C_{21}H_{28}N_2S_4$: C, 57.79; H, 6.42; N, 6.42%. Found: C, 57.51; H, 6.28; N, 6.32. MS (LC-MS/MS) m/z: 437 [M+1]$^+$.

2.3. Extraction method

An organic solution (10 mL) of ligand (7.5×10^{-5} M) and an aqueous solution (10 ml) containing 1.25×10^{-5} M picric acid and 1×10^{-2} M metal nitrate were placed in stoppered flask and shaken for 2 h at 25.0 ± 0.1 °C. This period of shaking was enough to estabilish equilibrium between the two phases. The resulting mixtures were allowed to stand for 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 the absorbance of picrate ion in the aqueous solutions. The extractability was calculated from Eq. (1).

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

where A_0 is the absorbance in the absence of ligand and A 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 concentration was from 2.5×10^{-6} to 7.50×10^{-5} M.

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

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

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 [13].

$$\log\left\{\frac{D}{[\mathrm{Pic}^{-}]^{n}}\right\} = \log K_{\mathrm{ex}} + m\ \log\,[\mathrm{L}] \tag{3}$$

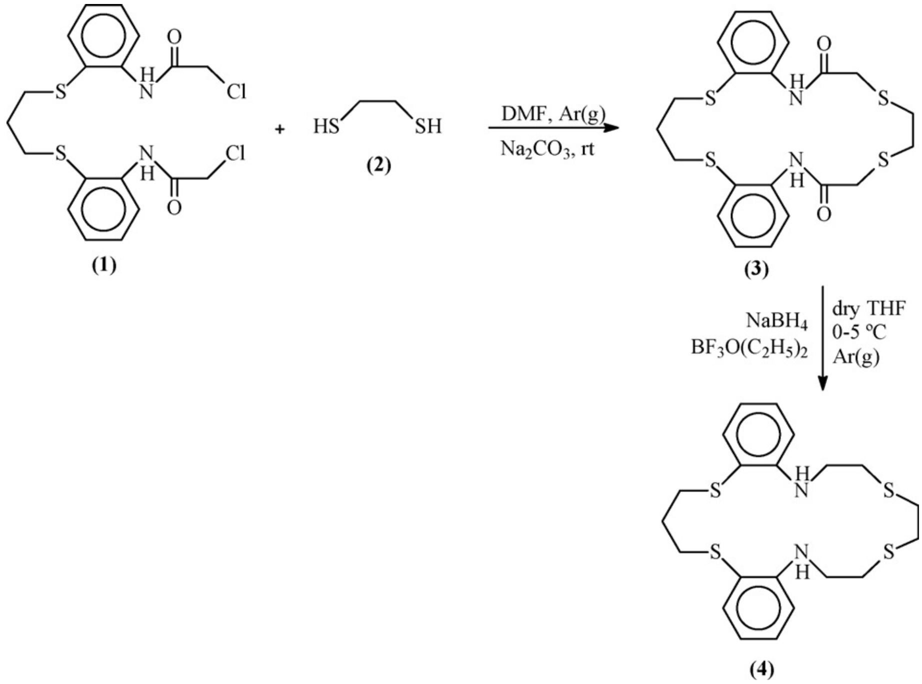
The plot of $\log\{D/[\mathrm{Pic}^-]^n\}$ as a function of $\log[\mathrm{L}]$ should give a straight line with a slope of m and $\log K_{\mathrm{ex}}$ can be calculated from the intercept by using Eq. (3).

3. Results and discussion

The preparation of two ligands containing nitrogen and sulfur donor atoms **3** and **4** is shown in Scheme 1. The structures of novel compounds were characterized by a combination of elemental analysis and ^{1}H NMR, ^{13}C NMR, MS spectral data. Compound **1** was synthesized according to reported procedures [12].

The reaction of N-[2-({3-[(2-aminophenyl)thio]prophyl}thio) phenyl]-2-chloroacetamide **1** [12] with ethane-1,2-dithiol **2**, fourfold excess of anhydrous K$_2$CO$_3$ in DMF at room temperature under argon atmosphere afforded 9,10,21,22-tetrahydro-5H,12H,20H-dibenzo[b,n][1,7,10,16,4,13]tetrathiadiazacyclononadecyne-6,13 (7H,14H)-dione **3** in 95% yield. The IR spectrum of compound **3** is almost identical to that of compound **1** with small changes in wavenumbers. The formation of macrocycle was confirmed by the appearance of a new resonance for SCH$_2$ protons at δ = 2.92 ppm as multiplet in the ^{1}H NMR spectrum of compound **3** in DMSO-d_6. The ^{13}C NMR spectrum of compound **3** indicated two new resonance for SCH$_2$ carbons between δ = 32.02 and 31.94 ppm when compared with the ^{13}C NMR spectrum of compound **1**. The mass spectrum of compound **3** displayed the expected molecular ion peak at m/z = 465 [M+1]$^+$.

The reduced macrocycle 6,7,9,10,13,14,21,22-octahydro-5H,12H, 20H-dibenzo-[b,n][1,7,10,16,4,13]tetrathiadiazacyclononadecyne **4** was obtained from the precursor α-bisamide macrocyclic compound **3** by using sodium boronhydride-boron trifluoride ethyl



Scheme 1.

etherate in dry THF at 0–5 °C under argon atmosphere in 79%. Analytical and spectroscopic data of compound **3** clearly confirmed the success of the reduction reaction. In the IR spectrum of compound **4**, the stretching vibrations belonging to C=O group in the precursor compound **3** were absent after the reduction reaction. The disappearance of the singlets at $\delta = 9.70$ and 3.45 ppm in the α-bisamide macrocyclic **4** and appearance of a singlet at $\delta = 5.44$ for –NH protons and a triplet at $\delta = 3.38$ ppm for $-NCH_2$ protons confirmed the proposed structure. The disappearance of the C=O signals, along with the appearance of a new peak at $\delta = 42.59$ ppm concerning NCH_2 group in the ^{13}C NMR spectrum of compound **4** can be taken as a clear evidence for the formation of reduced macrocycle. The expected molecular ion peak for compound **4** was observed at $m/z = 437$ $[M+1]^+$.

3.1. Extractability and selectivity

Transition metal picrates such as Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, and Pb^{2+} were used in extraction experiments. Two different organic solvents were tested to reveal the extraction efficiency of these metal cations from aqueous phase to organic phase at 25 ± 0.1 °C. These solvents were dichloromethane and chloroform.

The extractability of above metal picrates from the aqueous phase into the organic phase by ligands **3** and **4** is given in Table 1. The *E*% values, which are left, were obtained when dichloromethane was used as organic solvent. As seen from these parts, ligand **3** extracted only Ag^+ and Hg^{2+} ions effectively between the tested metal cations. The other values were below 1.0%. The highest *E*% value was obtained for Ag^+ ion with 48.3 in this case. The *E*% value for Hg^{2+} ion was 33.6%. Namely, ligand **3** shows high selectivity but moderate extractability toward these cations. The high selectivity may depend on conformational rigidity of the ligand because of diamide groups. Ligand **4,** which is more flexible extracted Cu^{2+} with 32.6%, Ni^{2+} with 10.8%, and the other metal cations below 4.4. This results from structural flexibility of the reduced compound. As known, conformational rigidity or flexibility of macrocycles has an important effect on their selective behavior [14]. The highest *E*% value belongs to Ag^+ ion with 96.2% for the ligand **4**. However, ligand **3** extracted the same ion 48.3% to dichloromethane. It is clear that the extractability results of the ligands are different. The *E*% values, which are right, were obtained when chloroform was used as organic solvent. Ligand **3** extracted Ag^+ ion 30.3% to the chloroform phase. This value was lower than that of dichloromethane. However, the ligand extracted Hg^{2+} ion 55.3% to chloroform and this value was higher than that of dichloromethane. This result shows that solvent is an important factor in extraction efficiency. We obtained similar results for Hg^{2+} ion in previous studies for the similar amide compound carrying one more sulfur donor atom [12]. In the study the extractability of Hg^{2+} ion was higher for chloroform with respect to dichloromethane. These results may depend on good solvation of ligand- Hg^{2+} picrate association with chloroform. As seen from the table, the extractability of Hg^{2+} and Ag^+ ion is different for both solvents. Ag^+ is extracted more than Hg^{2+} with the ligands except for compound **3** in case of chloroform. Similarly, we obtained the more Ag^+ extractabilities with respect to that of

Table 1

The extractability of aqueous metal picrates for compound (**3**) and (**4**) into organic phase[a]

Metal ion	Extractability[b] (%)		Extractability[c] (%)	
	(**3**)	(**4**)	(**3**)	(**4**)
Ag^+	48.3	96.2	30.3	93.5
Hg^{2+}	33.6	25.3	55.3	25.7
Cd^{2+}	<1.0	4.2	2.1	<1.0
Zn^{2+}	<1.0	<1.0	<1.0	<1.0
Cu^{2+}	<1.0	32.6	<1.0	5.8
Ni^{2+}	<1.0	10.8	<1.0	<1.0
Mn^{2+}	<1.0	3.4	<1.0	<1.0
Pb^{2+}	<1.0	4.0	<1.0	8.5
Co^{2+}	<1.0	4.4	1.1	6.1

[a] Temperature: 25.0 ± 0.1 °C; aqueous phase (10 mL); $[pic^-] = 1.25 \times 10^{-5}$ M, organic phase (10 mL); $[L] = 7.5 \times 10^{-5}$ M; The values calculated from three independent extraction experiments.

[b] Organic solvent: dichloromethane.

[c] Organic solvent: chloroform.

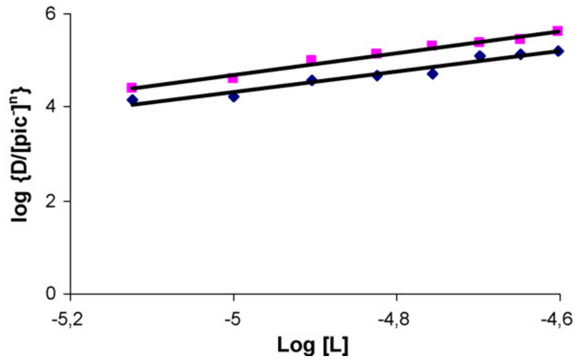


Fig. 1. $\log\{D/[\text{Pic}^-]^n\}$ versus log [L] for the extraction of Ag-picrate with ligand (**4**). (■) chloroform, (♦) dichloromethane.

Table 2
The relationship between composition and extraction constant for the ligand (**3**) and (**4**)–Ag^+ complexes

Solvent	Extraction constant $\log K_{ex}$		Complex composition L:M	
	(**3**)	(**4**)	(**3**)	(**4**)
Dichloromethane	11.28	16.32	3 : 2	2:1
Chloroform	11.20	15.20	3 : 2	2:1

Hg^{2+} in previous studies for the macrocyclic crown ligands with sulfur–nitrogen mixed donor atoms [12,13]. In this study ligand **4** shows a high extractability for Ag^+ with 93.5% over other cations. This value is near to that of dichloromethane. The ligand extracted Hg^{2+} ion 25.7% to chloroform. The values which belong to the other cation were below 8.5%.

Fig. 1 shows the evolution of $\log\{D/[\text{Pic}^-]^n\}$ when increasing the concentration of ligand **4** at constant Ag-picrate concentration with two different organic solvents. As seen from the plots, there is a linear relationship between $\log\{D/[\text{Pic}^-]^n\}$ and $\log[\text{L}]_{\text{org}}$, and the slope should be equal to the number of ligand molecules per cation in the extracted species. The slopes of lines are equal to 2.1 and 2.3 for dichloromethane and chloroform, respectively. Therefore, ligand **4** forms a 2:1 (L:M) complex with Ag^+ for both solvents. There was not a linear relationship between $\log\{D/[\text{Pic}^-]^n\}$ and $\log[\text{L}]_{\text{org}}$ for Hg^{2+} ion with the same ligand when both chloroform and dichloromethane were used as organic solvents. Similarly, we tested to calculate the complex composition and the $\log K_{ex}$ value for Cu^{2+}-ligand **4** complex. But we could not calculate it because of irregular evolution in the case of dichloromethane and chloroform. We investigated the complex composition of extracted species and $\log K_{ex}$ values for Hg^{2+} and Ag^+ ions with ligand **3**. The lack of a linear relationship was also present with ligand **3** for Hg^{2+} as with ligand **4**. In the case of Ag^+ case, the slopes were 1.5 and 1.6 for dichloromethane and chloroform, respectively. This result shows that ligand **3** forms the 3:2 complex with Ag^+ for both solvents.

The composition of extracted Ag-complexes for the ligands and their $\log K_{ex}$ values for the both solvents are given in Table 2. Ligand **3** gives the 3:2 complexes with Ag^+ for the both solvents. The $\log K_{ex}$ values were close in this case. Table 2 shows the composition of extracted complexes for ligand **4** and their $\log K_{ex}$ values for the both solvents. Ligand **4** gives the 2:1 sandwich complexes with Ag^+. The $\log K_{ex}$ values in the extraction of Ag^+ were 16.32 and 15.20 for dichloromethane and chloroform, respectively. The results in Table 2 show that dichloromethane was a more suitable solvent in comparison to chloroform for the transport of Ag^+ from aqueous phase to organic phase.

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