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Evaluation of Mononuclear Ni(II) Complex of a Tetra-cryptanded Vic-dioxime and its Model Compound 14-Membered $N_2O_2S_2$-Macrobicyclic Ligand as Pb^{2+}, Cd^{2+}, and Hg^{2+} Extractants

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Abstract: A macrobicyclic ligand and its mononuclear Ni(II) complex were studied as extractants for Pb^{2+}, Cd^{2+}, and Hg^{2+}. The metal picrates were used for extraction experiments. The solutions of the ligands in chloroform and dichloromethane were used as organic phases. The most effective transport was observed for Cd^{2+} picrate among the tested metal picrates with dichloromethane. The effect of pH on the extraction efficiency was evaluated for both organic solvents. The cations were stripped from the organic phase with 0.75 M nitric acid and the ligands were determined spectrophotometrically in the proper wavelength. The recovery% values of the ligands were calculated at pH 3.5.

Keywords: Macrobicyclic ligand, metal complexes, solvent extraction, toxic metal cation

INTRODUCTION

Interaction of macrocyclic ligands with metal cations is important for many analytical chemists since this type of interaction allows solving the various separation and determination problems related with metal

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cations. Hence, crown ether macrocycles carrying oxygen, nitrogen, and sulfur donors have been studied for many years (1–5). It has been shown that crown ether ligands can be used as effective extractants in separation of the toxic metal cations from aqueous media (6–9).

The solvent extraction method has been used in the investigation of extraction properties of macrocyclic ligands. The advantage of this method is the simplicity of the extraction techniques. Moreover the method provides determination of the possibility of selective complexation for a certain cation. Metal cation is transported from aqueous media in the form of ion associations. The cation is located in the cationic part of the ion association. A bulky and easily polarizable anion such as a picrate is used in the effective extraction of ion associations. The stability of the formed complex between macrocycle and metal cation is important in the effective transport of the metal cation from aqueous media to organic media. Because of this, macrocyclic chemists endeavor to find a stable cation-macrocycle combination during the improvement of effective extractants.

Macrobicyclic ligands, known as cryptands, form more stable complexes with metal cations due to "cryptat effect" with respect to macrocyclic ligand (10). However, there are a limited number of examples of macrobicyclic ligand as an effective extractant in the literature (11). On the other hand, these are generally mono-cryptand ligands. There is no investigation on the extractant properties of the molecules consisting of more than one macrobicyclic moieties. Such bulky molecules consisting of macrocyclic crown ether moieties have been investigated as extractants for metal cations. Bartsch and Lindoy have investigated the extraction properties of such type of macrocyclic ligand for alkali and transition metal cations (12–13). Recently, we have investigated extraction properties of di- and tetra-crowned molecules with oxygen and sulfur donor atoms for transition metal cations (14).

In the continuation of our interest in the extractant properties of the bulky molecules carrying more than one macrocyclic cavity in the structure, we investigated the extraction efficiency of 14-membered macrobicyclic ligand with nitrogen-oxygen-sulfur mixed donors with that of the corresponding tetra-cryptanded molecule depending on pH. Our aim was to investigate the extraction properties of the bulky Ni-complex carrying four dioxadiazadithiamacrobicycle (**2**) according to the model compound (**1**) for toxic metal cations such as Pb^{2+}, Cd^{2+}, and Hg^{2+}.

EXPERIMENTAL

Macrobicyclic ligands (**1**) and (**2**) were synthesized in our laboratory according to the procedure described previously (15). $Pb(NO_3)_2 \cdot H_2O$,

$Cd(NO_3)_2 \cdot 4H_2O$, $Hg(NO_3)_2 \cdot H_2O$, HNO_3, CH_3COOH, CH_3COONa, chloroform, dichloromethane, and picric acid were the analytical grade 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 spectrophotometric measurements were carried out with a Unicam UV2 UV-visible spectrophotometer. In solvent extraction experiments Edmund Bühler KS-15 type shaker was used. A Jenway 3040 Ionalyzer was used for adjusting the pH of metal picrate solutions.

Extraction Method

Extraction experiments were performed according to the published procedure (14). Transition metal picrates were prepared by the stepwise addition of a 1×10^{-2} M of metal nitrate solution to a 3×10^{-5} M aqueous picric acid solution and shaking at 25°C for 1 h. An organic solution (10 mL) of ligand (5.5×10^{-5}M and 1.1×10^{-5}M for 1 and 2, respectively) and an aqueous solution (10 mL) containing metal picrate (3.0×10^{-5}M) were placed in a stoppered flask, and shaken for 8 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. For investigation of the effect of pH on % E, the aqueous solution was buffered to pH 1.9, 2.9, and 3.5 (0.01 M $NaNO_3/HNO_3$) and pH 4.0, 4.3, and 5.0 (0.01 M CH_3COONa/CH_3COOH). 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 determination of extractability is based on the absorbance of picrate ion in the aqueous solution. The extractability was calculated from Equation (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.

Stripping Procedure

After the extraction of the aqueous phase, the organic phase was evaporated under reduced pressure. The residue was treated with 10 mL of 0.75 M HNO_3 for stripping the metal cation at 40°C for 1 h. The aqueous solution was extracted with 10 mL of chloroform. The chloroform phase was used for the determination of the ligand concentration with UV-vis spectrophotometer using calibration graphic. The measurements were carried out at 347 and 257 nm for ligands (**1**) and (**2**), respectively. Recovery % was calculated according to Equation (2).

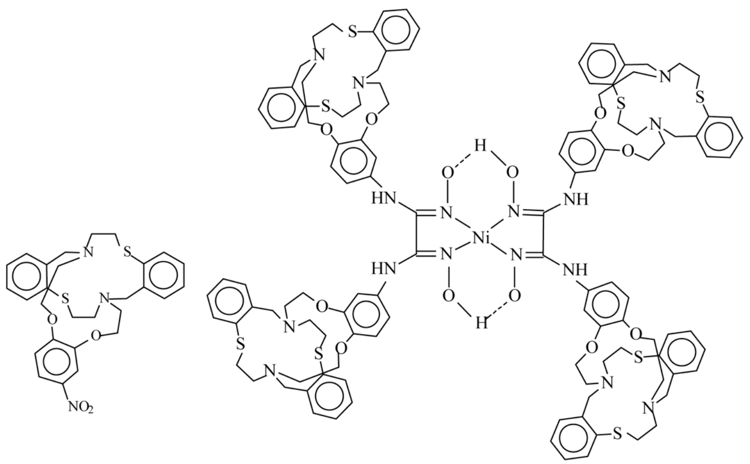
$$R(\%) = (C_2/C_1) \times 100 \tag{2}$$

C_1 is the ligand concentration before extraction. C_2 denotes the ligand concentration after extraction.

RESULTS AND DISCUSSION

The structure of the ligands (**1**) and (**2**) used in this study are shown in Fig. 1. Extraction data were obtained by using chloroform and dichloromethane solutions of the ligands to transfer metal picrates from aqueous solution. The equilibrium concentration of picrate in aqueous solution was then determined spectrophotometrically.

Table 1 shows the extractability of Pb^{2+}, Cd^{2+}, and Hg^{2+} picrates from the aqueous phase into the organic phase by compound (**1**) and compound (**2**). When chloroform was used as an organic solvent, compound (**1**) extracted all the cations nearly with the same E % values, which were between 18% and 15%. It is clear that compound (**2**) showed



(1) **(2)**

Figure 1. Extractants used for this study.

Table 1. The extractability of aqueous metal picrates for compound (**1**) and (**2**) into organic phase[a]

Metal ion	E (%) Chloroform		E (%) Dichloromethane	
	(**1**)	(**2**)	(**1**)	(**2**)
Pb^{2+}	18 ± 0.4	56 ± 1.1	38 ± 0.6	72 ± 0.9
Hg^{2+}	17 ± 0.3	58 ± 0.7	35 ± 0.4	67 ± 0.8
Cd^{2+}	15 ± 0.6	28 ± 0.6	31 ± 0.2	78 ± 1.2

[a] Temperature: 25.0±0.1°C; pH = 4.0; aqueous phase (10 mL); $[\text{pic}^-] = 6.0 \times 10^{-5}$M, organic phase (10 mL); $[L] = 5.5 \times 10^{-5}$ M and 1.1×10^{-5} M for (**1**) and (**2**), respectively; Defined as percent picrate extracted into the organic phase. The values and standard deviations calculated from three independent extraction experiments. The values are mean values.

higher extraction for the metal ions, where Pb^{2+} and Hg^{2+} picrates were extracted 56% and 58% to chloroform with compound (**2**), respectively. However, the Cd^{2+} extractability result for ligand (**2**) is lower than those of Pb^{2+} and Hg^{2+}, since Cd^{2+} picrate was only extracted 28 %. As seen from Fig. 1, compound (**2**) has four macrobicyclic moieties and it is expected to transport metal cations more effectively with respect to compound (**1**). The results in Table 1 show that the percentage of the extraction of all the metal ions with compound (**2**) is higher than that of compound (**1**) for both organic solvents. Also, it is clear that dichloromethane is a more proper solvent in the effective extraction of the cations. As seen from the table, compound (**1**) extracted all the cations to the dichloromethane phase with nearly the same E% values, which were in the range 38–31%. However, the percentage of the extraction of all the metal ions with compound (**2**) is higher than that of compound (**1**) for the same solvent. The highest extractability % belongs to Cd^{2+} ion for dichloromethane with compound (**2**). The value of extractability % is 78 in this case. It is interesting that the lowest extractability % belongs to Cd^{2+} ion for chloroform with the same ligand. The value of extractability % is 28 in this case. These results show that organic solvent is very important in extraction efficiency. Similar results were obtained for some macrocyclic ligands carrying nitrogen-sulfur mixed donor atoms (16–17).

It is well known that sulfur and nitrogen donor atoms in the macrocycles prefer soft metal cations such as Hg^{2+}, Cd^{2+} in complexation (18). In the present study, macrobicyclic ligands with nitrogen-sulfur-oxygen donor atoms were tested. As known, oxygen donor atoms are harder with respect to nitrogen donor atoms. Therefore, we can expect that the presence of oxygen donors in addition to nitrogen and sulfur donors

Table 2. The ligand recovery from the chloroform phase including the ion association[a]

	Recovery (%)	
Metal ion	(**1**)	(**2**)
Pb^{2+}	77 ± 1.9	67 ± 0.6
Hg^{2+}	50 ± 0.9	33 ± 0.7
Cd^{2+}	48 ± 0.4	52 ± 0.9

[a]Temperature: 25.0±0.1°C; Stripping agent: 0.75 M HNO_3, pH = 3.5. The values and standard deviations calculated from three independent extraction experiments. The values are mean values.

in the macrobicyclic cavity causes less stable Hg^{2+} and Cd^{2+} complexes. Since Pb^{2+} is a harder metal cation compared to these cations, the presence of hard oxygen donor atoms causes good extraction efficiency for this cation. Similar results were obtained for Pb^{2+} with compound (**1**) in different extraction condition in the previous study (19).

Table 2 shows the recovery of ligands after extraction, where 0.75 M HNO_3 was used as stripping agent. As seen from the table, the recovery % values are different for each metal cation extraction. The best recovery was obtained for Pb^{2+} in case of both ligands. Ligand (**1**) can be recovered 77% after the extraction of Pb^{2+}, whereas ligand (**2**) can be recovered 67%. Ligand (**1**) can be recovered 50% after the extraction of Hg^{2+} whereas ligand (**2**) can be recovered 33%. These results show that the stripping of Pb^{2+} and Hg^{2+} from the bulky molecule ligand (**2**) is more difficult with respect to model compound (**1**). This may result from more stable ion associations in case of ligand (**2**). However, ligand (**1**) can be recovered 48% after the extraction of Cd^{2+} whereas ligand (**2**) can be recovered 52%. These results show that the effective recovery of ligand also depends on the type of metal cation.

In this work, the effect of varying pH upon extraction capability of Pb^{2+}, Hg^{2+}, and Cd^{2+} cations by using the ligands was investigated. The results obtained are given Figs. 2, 3 and 4. Figure 2(a) shows pH dependence for Cd^{2+} extraction when chloroform was used as organic solvent. The highest E% value is 30 at pH 2.9 for compound (**1**) in extraction with chloroform. The value of related to compound (**2**) is 33% at the same pH. However, compound (**2**) extracted Cd^{2+}most effectively at pH 3.5 with 40%. As seen from Fig. 2(b), Cd^{2+} was transported to dichloromethane with a percentage of 31% and 78% by compound (**1**) and compound (**2**) at pH 4.0, respectively. On the other hand, the highest E%

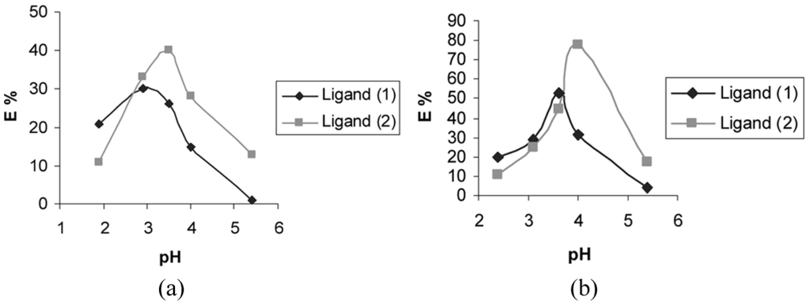


Figure 2. pH dependence for Cd^{2+} extraction. (a) organic phase, chloroform. (b) organic phase, dichloromethane.

value is 53 at pH 3.6 for compound (**1**) in extraction with dichloromethane. When Fig. 2(a) and Fig. 2(b) are compared, it is clear that dichloromethane is a better organic solvent than chloroform in the extraction of Cd^{2+}.

Figure 3(a) shows pH dependence for Pb^{2+} extraction when chloroform was used as organic solvent. At pH 3.0, the highest E% value is 44 for compound (**1**) in extraction with chloroform. The value of related to compound (**2**) is 35% at the same pH. However, compound (**2**) extracted Pb^{2+} more effectively at pH 4.0 with 56%. When chloroform was used as organic solvent at pH 4.0, as seen in Fig. 3(a), Pb^{2+} was extracted to chloroform with a percentage of 18% by compound (**1**) and for compound (**2**), the highest extractability value (i.e. 56%) was obtained. However, for compound (**1**) the highest E% (i.e. 44%) was obtained at pH 3.0 with chloroform. Figure 3(b) shows pH dependence for Pb^{2+} extraction when dichloromethane was used as organic solvent. As similar to the

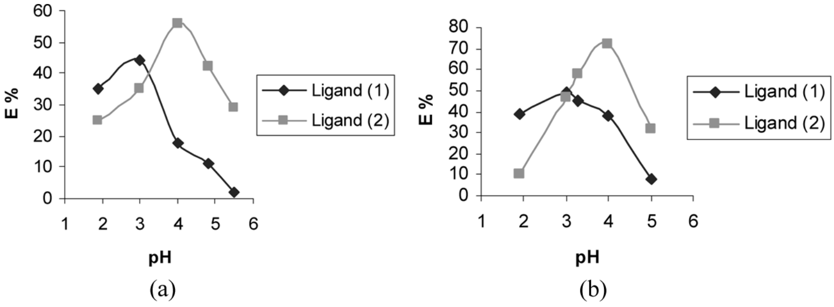


Figure 3. pH dependence for Pb^{2+} extraction. (a) organic phase, chloroform. (b) organic phase, dichloromethane.

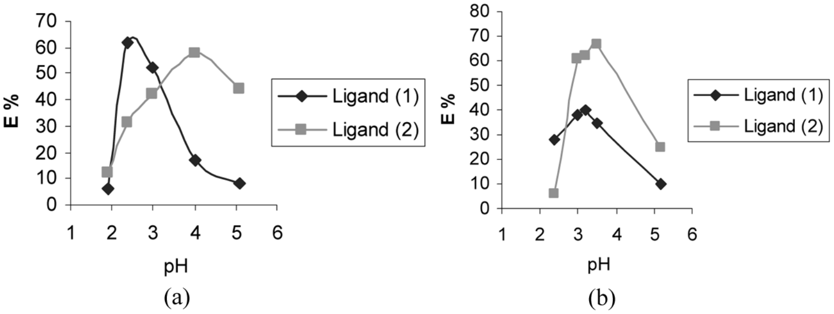


Figure 4. pH dependence for Hg^{2+} extraction. (a) organic phase, chloroform. (b) organic phase, dichloromethane.

extraction of Cd^{2+}, the extractability values increased for Pb^{2+} in the extraction with dichloromethane. Pb^{2+} was extracted to dichloromethane with a percentage of 49% at pH 3.0 and 56% with compound (**1**). However, compound (**2**) extracted the same cation at pH 4.0 with 72%.

Figure 4(a) shows pH dependence for Hg^{2+} extraction when chloroform was used as organic solvent. At pH 2.4, the highest E% value is 62 for compound (**1**) and 31 for compound (**2**). However, compound (**2**) extracted Hg^{2+} most effectively at pH 4.0 with 58%. It is interesting that the model compound (**1**) is a more effective extractant when chloroform was used as organic solvent. The investigation of pH dependence of Hg^{2+} extraction when dichloromethane was used as organic solvent (see Fig. 4(b)) revealed that similar to the extraction of Pb^{2+}, the extractability values of compound (**2**) are higher than that of compound (**1**) between pH 3.0 and 5.0. Similar manner is valid for Cd^{2+} in the pH range 4.0–5.0 when the same solvent was used. As seen from Figs. 2(a), 3(a), and 4(a), compound (**2**) extracted all the metal cations to chloroform more effectively than compound (**1**) between pH 3.5 and 5.0.

Consequently, it is shown that compound (**2**) can be used as an effective extractant in the extraction of such as Hg^{2+}, Cd^{2+}, and Cd^{2+} toxic metal cations. Dichloromethane is an effective organic solvent in liquid-liquid extraction. The speed in attaining of the equilibrium of the extraction with compound (**2**) is also an advantage.

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