



Evaluation of Diazatetraoxa Cryptand as Extractant for Transition Metals and Pb²⁺

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Abstract

The extractability of metal cations such as Mn²⁺, Co²⁺, Cu²⁺, Zn²⁺ and Pb²⁺ from aqueous phase to organic phase with 19-nitro-6,7,15,16,23,24-hexahydro-13H,26H-14,25-propanotribenzo-[b,l,o][1,4,11,14,7,18]-tetraoxadiazacyclokocine was investigated by means of UV-vis spectrophotometer. The aqueous phase and the organic phase contained metal picrate and the ligands, respectively. Chloroform and dichloromethane were the organic solvents. The effect of pH on the percent extraction was evaluated between 2.0 and 5.5 for both organic solvents. The range at which high percent extraction of the ligand was obtained was between pH 5.0 to 5.5 for both solvents. The most effective transport was observed for Mn²⁺ with 84.69 % picrate among the tested metal picrates with dichloromethane at pH 5.5. The extraction constant values (log K_{ex}) were determined for extracted metal complexes at the most effective extraction pH.

Keywords: Metal picrate; Cryptand; Transition metal cation; Solvent extraction.

Introduction

The cation selectivity of macrocyclic ligands such as crown ether and cryptands makes them excellent candidates for analytical applications. Interaction of crown ethers with metal cations has been investigated since 1970s. Also, cryptands form more stable complexes with metal cations with respect to crown ether. It is called "cryptat effect" [1-2]. There are many studies on cation-cryptand complexation [3-7] reported in the literature. For example, kryptofix 222 having nitrogen and oxygen donor atoms has drawn interest due to % its ability to selectively bind ions, especially alkali and alkaline earth metal cations [8-10]. Also, the investigations on cryptands with mixed donor are not competent enough to disclose the effective extractants for metal cations [11-13].

Solvent extraction has been used to figure out the properties of metal-macrocyclic interaction for many years because of its cost-effectiveness

and simplicity [14-16]. The need for selective reagents and processes for species with similar chemical properties still renders the investigations on the interaction of metal cations with macrocyclic ligands. It is well known that the extractability of metal ions with macrocyclic reagents such as *crown ether and cryptand* is governed by the stability of the metal complexes [17]. However, conditions including pH, nature of solvent, counter anion used, extractant concentration, stripping agent, interferences are effective in selective extraction for metal ions.

The influence of metal ions on the spectroscopic properties of macrocyclic ligands has been generally investigated by UV-vis absorption spectrophotometry and sometimes by fluorescence emission spectroscopy. Pedersen's procedure is suitable for determination of extraction properties of such type of ligands for metal ions [18]. For this purpose, picrate was used

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as a counter ion to measure absorbance of aqueous phase after extraction. The bulky picrate ion allows transport of metal ion from aqueous phase to organic phase. In addition it is being used as a color ion to measure absorbance by UV-vis spectrophotometer.

Previous researches on the macrocyclic ligands have provided insight into the interaction of metal cations with crown and cryptand ethers containing mixed donor atoms. Solvent extraction has been used for the reason mentioned above in these investigations. In earlier studies, the extractant properties of some crown ether macrocycles carrying oxygen, nitrogen and sulfur donors has been investigated and the results disclosed selective crown ethers for some transition metal cations such as Ag^+ and Hg^{2+} . In this paper, we present extraction properties of a cryptand ligand with oxygen and nitrogen donor atoms for some first row transition metals and Pb^{2+} depending on pH.

Experimental

Materials and reagents

19-nitro-6,7,15,16,23,24-hexahydro - 13H, 26H-14,25-propanotribenzo-[b,l,o] [1,4,11,14,7, 18]-tetraoxadiazacyclokocine was synthesized in our laboratory according to the procedure described previously [19]. Picric acid, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, HNO_3 , NaNO_3 , CH_3COOH , CH_3COONa , dichloromethane and chloroform were purchased from Merck. All of them were analytical grade reagents. Demineralized water was used to prepare the aqueous solutions. To prevent volume changes of the phases the solvents were saturated with each other before use.

Instrument

Thermo Scientific Evolution 6 spectrophotometer was used with a quartz cell of 1-cm pathlength for the spectrophotometric measurements. Edmund Bühler KS-15 type shaker was used in the extraction experiments. To adjust pH of metal picrate solutions Jenway 3040 Ionalyzer was used.

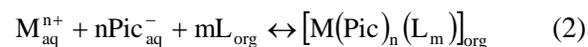
Extraction method

To determine complex composition, an organic solution (10 mL) of ligand **1** ($1.0 \times 10^{-6} \text{ M}$ - $2.9 \times 10^{-5} \text{ M}$) and an aqueous solution (10 mL) containing $1.0 \times 10^{-5} \text{ M}$ picric acid and $1.0 \times 10^{-2} \text{ M}$ metal nitrate were placed in a stoppered flask, and shaken for 15 min at $25 \pm 0.1^\circ\text{C}$. The mixture was allowed to settle for two hours for the completion of phase separation. The pH of aqueous solutions was maintained to pH 2.0, 2.5, 3.0, 3.5 ($0.01 \text{ M NaNO}_3/\text{HNO}_3$), 4.0, 4.5, 5.0 and 5.5 ($0.01 \text{ M CH}_3\text{COONa}/\text{CH}_3\text{COOH}$) using buffer solutions to investigate the effect of pH on E %. Picrate and ligand concentrations were $5.0 \times 10^{-6} \text{ M}$ and $1.5 \times 10^{-4} \text{ M}$, respectively. The spectrophotometric absorbance measurements were carried out at 355 nm to determine the concentration of picrate ion in the aqueous phase after extraction. In the absence of the ligand there was no picrate extraction. The determination of extractability is based on the absorbance of picrate ion in the aqueous solution. The extractability was calculated from Equation (1):

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

Where A_0 and A represent the absorbance in the absence of ligand and in the aqueous phase after extraction, respectively.

The dependence of D upon the ligand concentration was examined. Where, D represents the distribution ratio of the cation between the aqueous phase and the organic phase. The ligand concentration was varied in the range of 2.5×10^{-6} to $7.5 \times 10^{-5} \text{ M}$. Equation 2 gives the general extraction equilibrium.



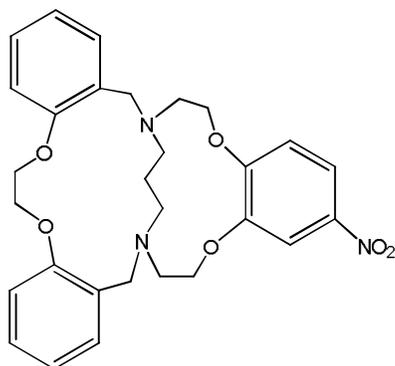
Where "aq" and "org" represent the aqueous and organic solution, respectively. Equation (3) is valid for the mentioned extraction system [20].

$$\text{Log} \left\{ \frac{D}{[\text{Pic}]^n} \right\} = \text{log } K_{\text{ex}} + m \text{log } [L] \quad (3)$$

The plot of $\text{log} \{D/[\text{Pic}]^n\}$ versus $\text{log } [L]$ should be a straight line with a slope of m . The intercept of the line equals to the $\text{log } K_{\text{ex}}$ value.

Results and Discussion

Structure of the ligand (**1**) is given in (Fig. 1). The solutions of (**1**) in chloroform and dichloromethane were used to transport metal picrates from aqueous solution. The concentration of picrate in aqueous solution was then measured spectrophotometrically.



(1)

Figure 1. Extractant used for this study

Shaking times of 15 min, 2h and 4h were tested to obtain a constant extraction percentage. (Fig. 2) shows the effect of shaking time on extraction capability of Cu^{2+} ion by using the ligand (**1**) at various pH. It can be observed that 15 min is enough to reach the equilibrium in the extraction of Cu^{2+} with the ligand (**1**). Similar results were obtained for other tested metal cations.

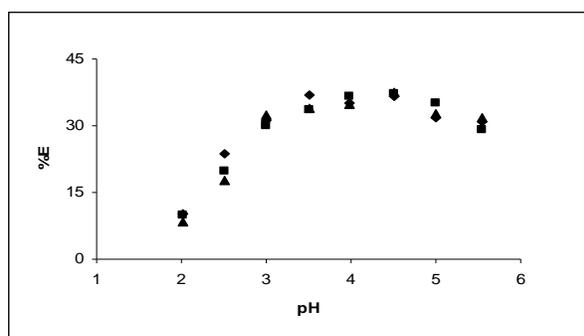


Figure 2. The effect of shaking time upon extraction of Cu^{2+} by using the ligand (**1**) at various pH values. \blacklozenge , \blacksquare and \blacktriangle represent shaking times of 15 min, 2h and 4h, respectively. $[\text{pic}^-] = [\text{L}] = 5.0 \times 10^{-6} \text{ M}$.

The effect of pH upon the extraction percentage of Mn^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} and Pb^{2+} was investigated and the results obtained are given (Fig. 3a). Fig. 3b shows the effect of pH on the

extraction of the metal complexes in case of chloroform. The highest E% value of about 80 % belongs to Cu^{2+} ions between pH 4.0 and 5.5. As seen from (Fig. 3b), E % values of Cu^{2+} are higher than those of Mn^{2+} , Co^{2+} , Zn^{2+} and Pb^{2+} between pH 3.5 and 5.5 in the case of chloroform, which is exactly the opposite of the results obtained with dichloromethane, where E % values of Cu^{2+} are lower than those of Mn^{2+} , Co^{2+} , Zn^{2+} and Pb^{2+} between pH 3.0 and 5.5. The extraction percentage of Cu^{2+} is about 60% between pH 4.5 and 5.5 when dichloromethane was used as organic solvent. This result shows that the extraction efficiency of Cu^{2+} ions decreased from about 80% to 60% at this pH range when the organic solvent changes from chloroform to dichloromethane.

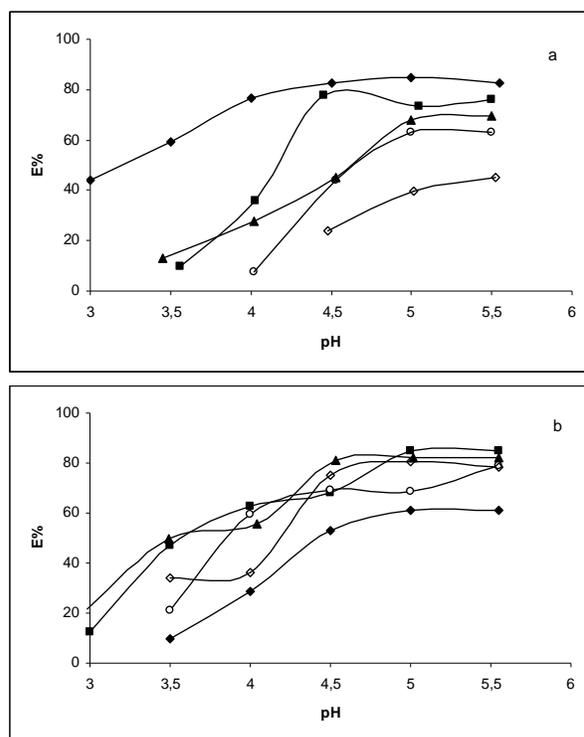


Figure 3a. The effect of pH on the extraction of the metal complexes. \blacklozenge , \blacksquare , \blacktriangle , \circ and \diamond represent Cu^{2+} , Mn^{2+} , Co^{2+} , Zn^{2+} and Pb^{2+} , respectively. b: chloroform, b: dichloromethane.

Our research group has investigated the solvent extraction properties of some macrocyclic crown ethers containing mixed donors for transition metals [21-25]. In these studies, we generally found that dichloromethane is more effective solvent than chloroform in the extraction of transition metal cations with macrocyclic crown ether carrying nitrogen-oxygen-sulfur mixed donor

atoms. In this study, we report similar results for macrobicyclic ligand carrying oxygen-nitrogen mixed donor atoms with tested transition metal cations and Pb^{2+} , except for Cu^{2+} , showing that the properties of Cu^{2+} -ligand (**1**) complex are different from those of other metal cations complexes. Higher extraction achieved for Mn^{2+} , Co^{2+} , Zn^{2+} and Pb^{2+} cations can be attributed to higher dielectric constant of dichloromethane. On the other hand, better solvation of the Cu^{2+} -ligand (**1**) complex by chloroform can be the reason for better extraction. As known, cryptand ligands show unusual extraction efficiency for metal cations [17]. Both the complex stability and distribution of the resulting complex in the organic phase are important for extraction efficiency.

The nitrogen donor atoms in the macrocycles prefer to moderate soft metal cations such as Mn^{2+} , Zn^{2+} , Co^{2+} and Cu^{2+} in complexation according to the concept of hard-soft acid base (HSAB) [26]. In this paper, the extractant properties of N_2O_4 type macrobicyclic ligand (**1**) with nitrogen-oxygen donor atoms were explained for first row transition metal cations and Pb^{2+} .

Table 1 shows the extractability of Mn^{2+} , Cu^{2+} , Co^{2+} , Zn^{2+} and Pb^{2+} picrates for ligand (**1**) into chloroform and dichloromethane phases at pH 5.5. Cu^{2+} was carried with the highest extraction efficiency i.e. 82.5% to the chloroform phase at this pH, whereas the lowest extractability belongs to Pb^{2+} ion which is 45.1%. Considering the chemical structure the more stable Cu^{2+} complex can be expected according to the concept of HSAB. The presence of oxygen donors in addition to nitrogen in the macrobicyclic cavity increases the hardness properties of donor atoms. The harder Cu^{2+} ion can form more stable complex with the ligand. The more stable complex causes the higher extraction efficiency for this cation in the case of chloroform. However, the complex stability may not be a valuable reason in effective extraction of metal cations with macrocyclic ligands. The effects such as distribution ratio of ligand and solvation of the complex by organic solvent are important in effective cation extraction with macrocyclic ligands [17]. The extractability for Pb^{2+} reaches 78.3% in the case of dichloromethane. Similar increases in the extraction % values were observed for other metal cations, except for Cu^{2+} ion, when

organic solvent changes from chloroform to dichloromethane at pH 5.5. As seen from (Table 1), the highest extractability belongs to Mn^{2+} ion with extraction of 84.7% for dichloromethane. It is clear that dichloromethane as compared to chloroform has more extraction efficiency in transport of metal ions, except for Cu^{2+} . However, chloroform is a more suitable solvent than dichloromethane for selective cation extraction.

Table 1. The extractability of aqueous metal picrates for ligand (**1**) into organic phase^a.

Metal ion	Extraction %	
	Chloroform	Dichloromethane
Mn^{2+}	75.9±0.9	84.7±0.6
Co^{2+}	69.9±1.5	82.3±0.3
Cu^{2+}	82.5±0.8	61.1±0.6
Zn^{2+}	63.0±1.0	79.0±0.8
Pb^{2+}	45.1±0.8	78.3±0.7

^aTemperature: $25.0 \pm 0.1^\circ\text{C}$; pH= 5.5; aqueous phase (10 mL); $[\text{pic}^-] = 5.0 \times 10^{-6}$ M, organic phase (10 mL); $[\text{L}] = 1.5 \times 10^{-4}$ M; The values were calculated from three independent extraction experiments

The ligand concentration effect on the distribution ratio was investigated at constant picrate concentration to determine the complex stoichiometry of extracted species. The plot of $\log \{D/[\text{Pic}^-]^n\}$ versus $\log [\text{L}]$ gives a straight line with a slope of $m \cdot \log K_{\text{ex}}$ value is the intercept of the line. In the case of chloroform, the evolution of $\log \{D/[\text{Pic}^-]^n\}$ when the concentration of ligand (**1**) is increased at constant picrate concentration is shown in (Fig. 4), and a slope value of 2.0 is obtained, showing that the complex composition of extracted species is 2:1(L:M) for Cu^{2+} ion.

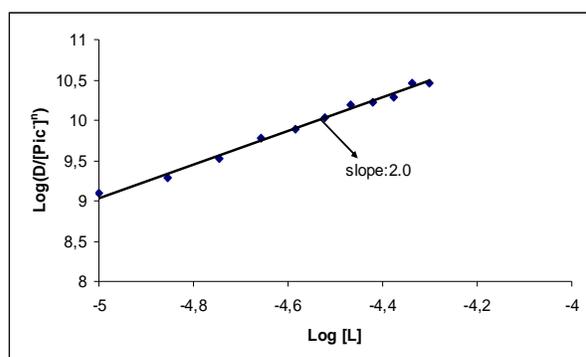


Figure 4. $\log \{D/[\text{Pic}^-]^n\}$ versus $\log [\text{L}]$ for the extraction of Cu^{2+} picrate to chloroform phase with ligand (**1**).

Table 2 gives the relationship between composition and extraction constants for the complexes of the ligand (**1**) for chloroform and dichloromethane. In the case of both organic solvents, the stoichiometry of extracted complexes was 2:1 (L:M) for Mn^{2+} , Zn^{2+} and Pb^{2+} ions, however, the stoichiometry was 3:2 (L:M) for Co^{2+} ion, which is an interesting finding. As seen from Table 2, Cu^{2+} was transported from aqueous phase to chloroform and dichloromethane phases as a 2:1 and 1:1 complex, respectively. This result shows importance of a solvent in the interaction of macrobicyclic ligands with metal cations. Accordingly, the extractant properties of cryptand ligands changed for metal cations. As seen from (Table 2), the $\log K_{ex}$ value of Cu^{2+} carried with a composition of 2:1 (18.38) is higher than that of 1:1 composition (16.07), suggesting that Cu^{2+} is carried more effectively to the chloroform phase with respect to dichloromethane. This result is in agreement with the results of Table 1. On the other hand, the values of $\log K_{ex}$ for Co^{2+} were 16.22 and 15.94 in chloroform and dichloromethane, respectively. The 2:1 complexes generally had high $\log K_{ex}$ values in the range of 17.86 and 21.14.

Table 2. The relationship between composition and extraction constants for the complexes.

Metal ion	Extraction constant		Complex Composition	
	$\log K_{ex}^a$	$\log K_{ex}^b$	L:M ^a	L:M ^b
Mn^{2+}	19.31	21.14	2:1	2:1
Co^{2+}	16.22	15.94	3:2	3:2
Cu^{2+}	18.38	16.07	2:1	1:1
Zn^{2+}	19.74	17.86	2:1	2:1
Pb^{2+}	20.40	20.00	2:1	2:1

^aOrganic solvent: chloroform

^bOrganic solvent: dichloromethane

Conclusion

Diazatetraoxa cryptand (**1**) effectively transported transition metals such as Mn^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} and Pb^{2+} from aqueous phase to organic phase. The highest extractability values were obtained at pH 5.5 and Mn^{2+} was also transported most effectively to dichloromethane phase at this pH. The percentage extractability value was 84.7 and accordingly the highest extraction constant ($\log K_{ex}$) value of 21.14 was obtained. The

composition of extracted complexes were 2:1 (L:M) for Mn^{2+} , Zn^{2+} and Pb^{2+} ions, however, such composition was 3:2 for Co^{2+} in both chloroform and dichloromethane.

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