# Transition Metal Ion-binding Properties of a 14-Membered $N_2O_2S_2$- Macrobicyclic Ligand

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## Abstract

The selective liquid–liquid extraction of various transition metal cations from the aqueous phase to the organic phase was carried out using a 14-membered $N_2O_2S_2$-macrobicycle. Metal picrates such as $Pb^{2+}$, $Co^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Cu^{2+}$ and $Cd^{2+}$ were used in this extraction studies. It was found that the ligand showed moderate selectivity towards $Pb^{2+}$ only among the other metals. The extraction constant (log $K_{ex}$) was determined to be 13.8 for $Pb^{2+}$ complex.

## Introduction

Industrial-based metallic contamination of the air, soil, and water supplies is a major environmental concern [1]. The toxic effects of many heavy metal ions such as $Hg^{2+}$, $Pb^{2+}$, $Cd^{2+}$ are well documented [2–5].

Especially, the toxic nature of lead and it's widespread occurrence in the environment has resulted in the search for effective and selective lead binding materials and ligand systems.

Macrocyclic multidentate ligands with an appropriate combination of ring size, identity and placement of donor atoms exhibit good extraction selectivity for desired metal ions [6]. 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, isotope separation [7–11].

The solvent extraction studies of alkali metals with macrocyclic polyethers, especially oxygen-containing compounds, were carried out with various crown ethers. The complexes formed by cryptands with metal ions are more stable than similar complexes of crown ethers, therefore cryptands can be more attractive ligands as selective extraction reagents. Generally, we can find some investigations on the transport of metal ions with known macrocyclic ligands such as [2.2.2]-cryptand, [2.2.1]-cryptand in the literature [12–13]. Whereas the similar studies with aza-thia or aza-oxa-thia macrobicyclic ligands are not sufficient.

The selectivity of alkali and alkaline earth metal ion extraction with macrocycles containing oxygen donor atom, primarily crown ethers, is correlated with its radius [14]. In metal extraction with macrocycles containing nitrogen–sulfur–oxygen donor atoms, many factors exert influence upon 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.

In the previous studies, we have investigated solvent extraction properties of some macrocyclic ionophores containing mixed donor atoms for heavy metals [15–16]. In this study, we presented solvent extraction properties of one of a series of macrobicyclic ligands with mixed donor atoms that were synthesized previously [17–19] for the transition metal cations such as $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Co^{2+}$, and $Cu^{2+}$. The results of solvent extraction experiments showed the moderate selective extraction of lead over other transition metals tested.

## Experimental

### Reagents and apparatus

7-Nitro-4,11-dioxa-22,32-dithia-1,14-diazapentacyclo [12.10.10.0$^{5.10}$ . 10$^{16.21}$ . 0$^{26.31}$] tetratri- aconta-5,7,9,16, 18,20,26,28,30-nonan were synthesized in our laboratory according to procedure described previously [17].

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Dichloromethane, picric acid, Pb(NO$_3$)$_2$, Cu(NO$_3$)$_2$, Zn (NO$_3$)$_2$, Ni(NO$_3$)$_2$, Cd(NO$_3$)$_2$, Co(NO$_3$)$_2$ were the analytical grade reagents. They were purchased from Merck. Demineralized water were used in 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 Unicam UV2 UV–visible spectrophotometer. In solvent extraction experiments Grant SS 30 type shaker with thermostat was used.

## Extraction method

A dichloromethane solution (10 mL) of ligand ($2.5 \times 10^{-4}$ M) and an aqueous solution (10 mL) containing $2.5 \times 10^{-5}$ M picric acid and $1 \times 10^{-2}$ M metal nitrate were placed in stoppered flask, and shaken for 1 h at $25.0 \pm 0.1$ °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 was determined based on the absorbance of picrate ion in the aqueous solutions and the efficiency was expressed as the distribution ratio ($D$). The distribution ratio of the bivalent metal ion may be represented by Eq. (1)

$$D = [MLA]_{org}/[M^{2+}]_{aq} \qquad (1)$$

where org and aq denote organic and aqueous phases, respectively. To characterize the extraction ability the dependence of the distribution ratio $D$ of the cation between the two phases upon the cryptand concentration was examined. The general extraction equilibrium is assumed to be given by Eq. (2)

$$M^{n+} + n \, Pic^-_{aq} + x \, L_{org} \rightleftharpoons [M \, (Pic)_n(L)_x]_{org} \qquad (2)$$
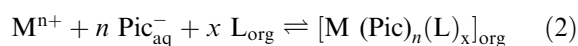
The overall extraction equilibrium constant is expressed as Eq. (3).

$$K_{ex} = \frac{[M(Pic)_n(L)_x]}{[M^{n+}][Pic^-]^n[L]^x} \qquad (3)$$

The distribution ratio $D$ would be defined by Eq. (4).

$$D = \frac{[M(Pic^-)_n(L)_x]}{[M^{n+}]} \qquad (4)$$

and the Eq. (5) can be obtained.

$$\log D = \log K_{ex} + n \log[Pic^-] + x \log[L] \qquad (5)$$

## Results and discussion

### Extractability and selectivity

Schematic representation of the ligand used in this study is shown in Figure (1). The cation binding ability of the cryptand ligand was assessed by solvent extraction of aqueous solution of bivalent metal picrates (cobalt, lead, cadmium, nickel, zinc, copper) at 25 °C with dichloromethane solutions of the ligand. The results of solvent extraction of these metal picrates from aqueous phase into dichloromethane phase with the ligand are summarized in Table 1.

As seen from Table 1, the ligand extracted each transition metal ion with different distribution ratio from the aqueous phase into the dichloromethane phase. The extractability of bivalent cation picrates were evaluated as a function of $[L]/[M^{2+}]$. Corresponding distribution ratios change between 0.028 and 1.671 for the tested transition metal ions at L/M = 1.0. The ligand has showed the highest extractability for Pb$^{2+}$. The distribution ratio is 1.671 in this case.

The complexation ability of the ligand with various transition metal ions may depend on its structural flexibility. In the previous study a detailed conformational analysis of the cryptand was made by using AMBER, MM2 and OPLS molecular mechanical methods, and its stable conformations were determined [20]. Both of them were depicted schematically in Figure 2. The ass (anti–syn–syn) conformation likes a basket and it is called as "basket" conformation. The another stable conformation which is aaa$^-$ (anti-anti-anti) type is called as "propeller" conformation. The difference between the stretching energies of the stable conformations of cryptand is little, and in certain condition, they may transform into each other. Namely, the transformation of the conformation of the cryptand from one form to another does not require too much energy, i.e. it is possible for the cryptand to easily change its conformation state during its interaction with metal ions.

The selected relative cation selectivities of Pb$^{2+}$/ Co$^{2+}$, Pb$^{2+}$/Cd$^{2+}$, Pb$^{2+}$/Ni$^{2+}$, Pb$^{2+}$/Zn$^{2+}$ and Pb$^{2+}$/
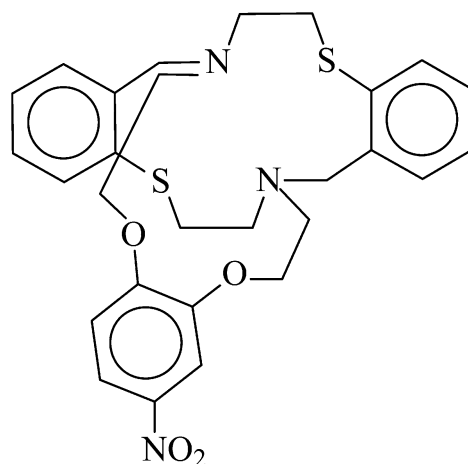


*Figure 1.* Extractant used for this study.

*Table 1.* Extractability of aqueous bivalent cation picrates by the ligand as a function of $[L]/[M^{2+}]$[a]

| L/M | Distribution ratios of bivalent cations $(D)$[b,c] | | | | | |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|
|     | $Pb^{2+}$ | $Co^{2+}$ | $Cd^{2+}$ | $Ni^{2+}$ | $Zn^{2+}$ | $Cu^{2+}$ |
| 0.2 | 0.162 | 0.013 | –     | 0.005 | 0.033 | 0.120 |
| 0.4 | 0.294 | 0.023 | 0.073 | 0.006 | 0.038 | 0.275 |
| 0.6 | 0.538 | 0.026 | 0.077 | 0.009 | 0.041 | 0.376 |
| 0.8 | 1.013 | 0.027 | 0.103 | 0.011 | 0.122 | 0.462 |
| 1.0 | 1.671 | 0.028 | 0.225 | 0.028 | 0.136 | 0.512 |
| 1.5 | 1.836 | 0.039 | 0.300 | 0.035 | 0.160 | 0.548 |
| 2.0 | 2.818 | 0.070 | 0.378 | 0.053 | 0.190 | –     |
| 3.0 | 3.749 | 0.110 | 0.457 | –     | 0.275 | –     |
| 5.0 | 6.854 | 0.327 | 1.490 | 0.532 | 0.363 | –     |

[a]Temperature, $25 \pm 0.1$ °C; aqueous phase, 10 mL; [picrates] $= 2.5 \times 10^{-5}$ M, organic phase ($CH_2Cl_2$), 10 mL.
[b]Defined as distribution ratio of cation between the organic and aqueous phases.
[c]Averages calculated from the data obtained from five independent extraction experiments.

$Cu^{2+}$ were calculated as $D_{Pb}{}^{2+}/D_M{}^{2+}$, where $D_{Pb}{}^{2+}$ and $D_M{}^{2+}$ represent the distribution ratio of $Pb^{2+}$ ion and $M^{2+}$ ion, respectively (Table 2). Also, the selectivity of bivalent cation picrates were evaluated as a function of $[L]/[M^{2+}]$. The ligand has showed the highest selectivity for $Pb^{2+}$ among the other used cations such as $Cd^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$ and $Cu^{2+}$. The selectivity of the ligand to $Pb^{2+}$ over the other cations is as follow at $L/M = 1.0$; $Pb^{2+}/Co^{2+} = 59.6$; $Pb^{2+}/Ni^{2+} = 59.6$; $Pb^{2+}/Zn^{2+} = 12.2$; $Pb^{2+}/Cd^{2+} = 7.4$; $Pb^{2+}/Cu^{2+} = 3.26$.

According to ion-cavity size concept it is estimated that the cryptand compound will exert a strong coordination force toward the transition metal ions $Cu^{2+}$, $Zn^{2+}$, $Ni^{2+}$ which have the ionic diameters of 1.64 Å, 1.66 Å, 1.50 Å, respectively, which are close to the cavity diameter of the cryptand [20]. However, the ligand

exhibited the highest selectivity for lead ion among the tested cations, which has a much larger ionic diameter (2.66 Å) than the cavity size of the cryptand (about 2.00 Å). This result shows that the ion-cavity size concept is not effective for the transition metals, which is in good agreement with literature findings [14]. The results can be explained with the HSAB concept rather than the size-fit effect because the softness of the nitrogen and sulfur atoms in the cryptand ligand cavity is similar to that of lead and cadmium cations. The other three cations are harder. As seen on Table 1, the results of the extraction capacity measurements of the ligand for almost all $[L]/[M^{2+}]$ values are in agreement with our explanations.

As seen from Eq. (5), a plot at constant [Pic⁻] of log $[D]$ versus log $[L]_{org}$ should be linear and its slope should be equal to the number of ligand molecules per cation in
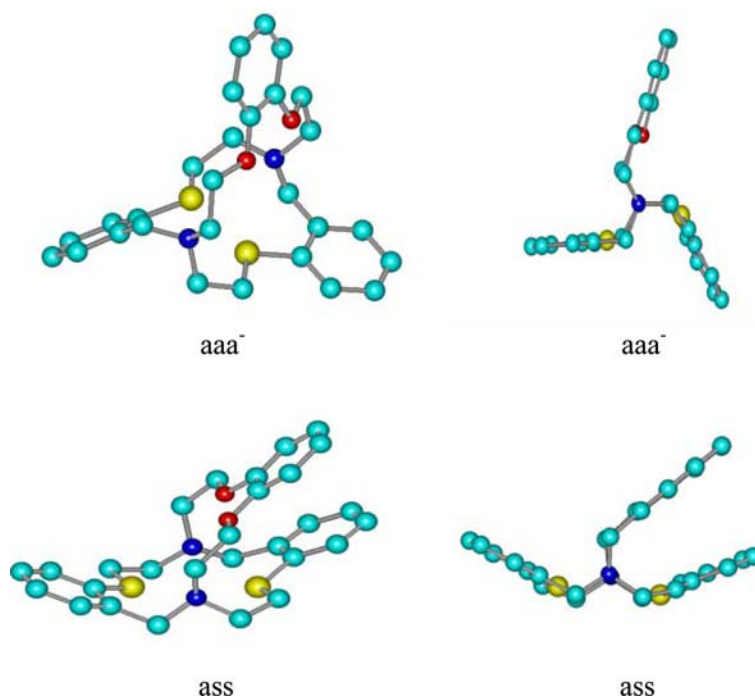


*Figure 2.* Schematic representations of two stable conformations of the cryptand. The images of the left and right are the images of the same conformation from different sides [20].

*Table 2.* Selectivity of $Pb^{2+}$ picrate compared to $Co^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Cu^{2+}$ and $Cd^{2+}$ picrates by the ligand as a function of $[L]/[M^{2+}]$

| L/M | $D_{Pb^{2+}}/D_{M^{2+}}$ | | | | |
|-----|--------------|--------------|--------------|--------------|--------------|
|     | $Pb^{2+}/Co^{2+}$ | $Pb^{2+}/Cd^{2+}$ | $Pb^{2+}/Ni^{2+}$ | $Pb^{2+}/Zn^{2+}$ | $Pb^{2+}/Cu^{2+}$ |
| 0.2 | 12.4 | –    | 32.4 | 4.9  | 1.35 |
| 0.4 | 12.7 | 4.0  | 52.5 | 7.73 | 1.06 |
| 0.6 | 20.6 | 6.9  | 59.7 | 13.1 | 1.43 |
| 0.8 | 37.5 | 9.8  | 92.0 | 8.3  | 2.19 |
| 1.0 | 59.6 | 7.4  | 59.6 | 12.2 | 3.26 |
| 1.5 | 47.0 | 6.12 | 52.4 | 11.4 | 3.35 |
| 2.0 | 40.2 | 7.45 | 53.1 |      | –    |
| 3.0 | 34.0 | 8.2  | –    | 13.6 | –    |
| 5.0 | 16.4 | 3.6  | 10.0 | 14.7 | –    |
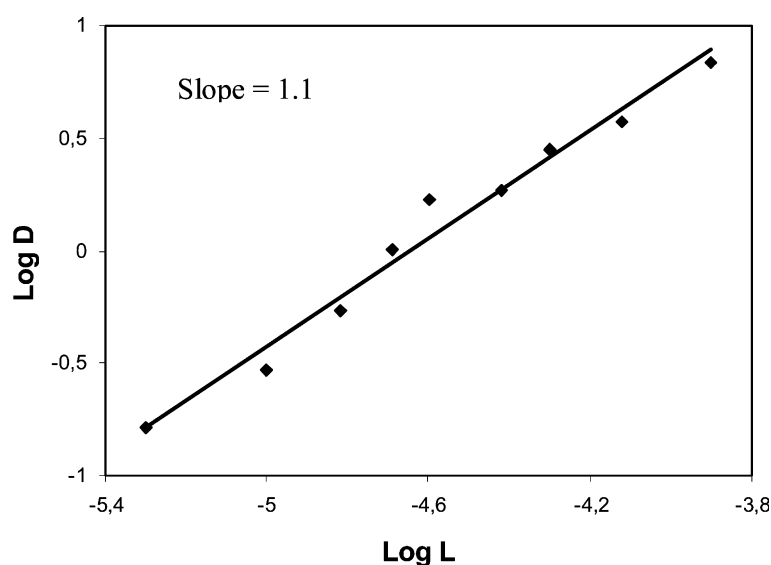


*Figure 3.* Plot of log $D$ versus log [L] for $Pb^{2+}$. [L]: ligand concentration, $D$: distribution ratio.

the extraction species. Figure 3. shows the extraction into dichloromethane at different concentrations of the ligand for $Pb^{2+}$. There is a linear relationship between log $D$ versus log [L]. The slope of line is equal to 1.1 suggesting that the ligand form a 1:1 complex with $Pb^{2+}$. The metal/ligand ratio determined by the molar-ratio method was also 1:1. The extraction equilibrium constant, $K_{ex}$, between an aqueous solution of $Pb(Pic)_2$ and a dichloromethane solution of the ligand can be obtained from the graph in Figure 3. and Eq. (5). Log $K_{ex}$ is 13.8 for the extraction of $Pb^{2+}$ with the ligand.

In this paper liquid-liquid extraction of selected transition metals with a macrobicyclic ligand was examined. The ligand showed moderate selectivity and extractability toward $Pb^{2+}$ ions. This phenomenon can be explained by the hard–soft acid–base principle.

The cation bonding properties of a mixed nitrogen–oxygen–sulfur donor macrobicyclic ligand were demonstrated by using solvent extraction method. The results of the extraction experiments is interesting with respect to macrobicyclic ligands designed for analytical purposes. Because there are no efficient investigations on demonstrating the effect of mixed donor atoms in

macrobicyclic ligands on the extraction of heavy metal picrates. This study is an example of the effect of mixed donor atoms in cryptands on the solvent extraction and it is important for further investigations in analytical macrocyclic chemistry.

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