

Interaction of the Post-transition Metal Ions and New Macrocycles in Solution

Oh-Jin Jung

Department of Environmental Science, College of Natural Science, Chosun University, Kwanju 501-759

Received February 15, 1993

Complexation of Cd^{2+} , Pb^{2+} and Hg^{2+} ions with four cryptands were studied by potentiometry and solution calorimetry in various weight percent methanol-aqueous solvent at 25°C under CO_2 free nitrogen atmosphere. The stabilities of the complexes were dependent on the cavity size of macrocycles. The Hg^{2+} ion stability constants are higher than those of Cd^{2+} and Pb^{2+} ion. All the cryptands formed complexes having 1:1 (metal to ligand) mole-ratio except for $\text{Hg}^{2+}\text{-}L_1$ (cryptand 1,2b: 3,5-benzo-9,14,17-trioxa-1,7-diazabicyclo-(8,5,5) heptadecane) and $\text{Cd}^{2+}\text{-}L_2$ (cryptand 2,2b: 3,5-benzo-10,13,18,21-tetraoxa-1,7-diazabicyclo (8,5,5) eicosane) complexes. $\text{Hg}^{2+}\text{-}L_1$ complex was a sandwich type, and the $\text{Cd}^{2+}\text{-}L_2$ complex showed two stepwise reactions. Thermodynamic parameters of the $\text{Cd}^{2+}\text{-}L_2$ complex were 6.08 ($\log K_1$), -7.28 Kcal/mol (ΔH_1), and 4.78 ($\log K_2$), -4.62 Kcal/mol (ΔH_2), respectively, for 1:1 and 2:1 mole-ratio. The sequences of the selectivity were increased in the order of $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$ ion for L_3 and L_4 macrocycles, and the L_2 -macrocycle has a selectivity for Cd^{2+} ion relative to Zn^{2+} , Ni^{2+} , Pb^{2+} and Hg^{2+} ions. Thus, it is expected that the L_2 can be used as carrier for separation of the post transition metals by macrocycles-mediated liquid membrane because L_2 is not soluble in water, and the difference of stability constants of the metal complexes with L_2 are large as compared with the other transition metal complexes. The ^1H and ^{13}C -NMR studies indicated that the nitrogen atoms of cryptands have greater affinity to the post transition metal ions than the oxygen atoms, and that the planarities of the macrocycles were lost by complexation with the metal ions because of the perturbation of ring current of benzene molecule attached to macrocycles and counter-anions.

Introduction

A large number of acyclic and bicyclic ligands possessing oxygen, nitrogen, sulfur and/or other donor atoms have been synthesized and their cation-binding behaviors has been investigated since the Pederson's first cyclic polyether, called crown ether. These synthetic ligands exhibit characteristic cation-binding behavior for alkali, alkaline earth metal ions, and heavy and transition metal ions.¹

The polyazamacrocycles behave as relatively strong bases in their first protonation steps and as weaker bases in the last protonation steps.² This grouping of the basicity constants is revealed in typical azamacrocycles, and has been explained in terms of charge-repulsion effects.^{3,4}

The possibility for these azamacrocycles to bind more than one metal ion in the macrocycle framework has arisen the curiosity of several research groups.

The work to date has been limited to macrocyclic complexes of the first row transition elements such as Zn^{2+} , Cu^{2+} and Ni^{2+} . Since second and third transition series elements are important as catalysts and some of the elements have large affinities for nitrogen, it is obvious that future works need to involve them.

Although many examples of synthetic macropolycyclic ligands are known, we need new preorganized receptors having even greater complex stabilities or higher selectivities for certain cations and neutral molecules. The reported examples of macrocyclic polyether have spherical, cylindrical basket, and folder shapes.⁵ It seems that nitrogen atoms are essential for the more complicated molecules to coordinate with transition metal ions. Cryptands, with nitrogen atoms at the bridgeheads, have 10^5 - 10^6 times greater association constants for certain cations than those with carbon atoms

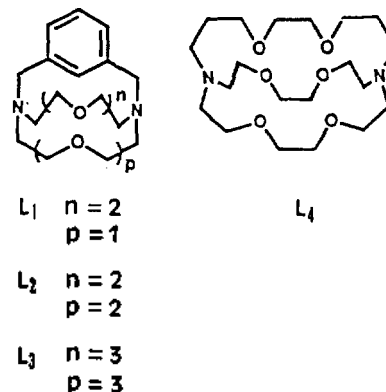


Figure 1. Structures of macrocycles.

at the bridgehead position.⁶

The post transition metal ions such as Cd^{2+} , Pb^{2+} and Hg^{2+} are very toxic. The design of highly selective ligands which are able to remove harmful cation is an interesting research subject, and we have need to separate the post transition metals like Cd^{2+} , Pb^{2+} and Hg^{2+} from other inorganic and organic substances for the control of toxic metal ions in the environment. Therefore, we have to measure the stability constant ($\log K$) for interaction of the ligands and metals.

In the present paper, we have synthesized new three macrocyclic compounds having nitrogen bridgeheads (Figure 1) and reasonable cavity size more closely matching the post transition metal cation, such as Cd^{2+} , Pb^{2+} and Hg^{2+} ions. We have discussed the interaction of the macrocycles and metal ions in solution, and we have observed process of the complexation and the mole ratios by using both potentiometry and solution calorimetry. We have also characterized st-

structures of the complexes in solution from the ^1H and ^{13}C -NMR spectra. We have also discussed the factors affecting the stability constants of these complexes.

Experimental

Materials. The crystalline solid of metal nitrates [Cd(II) from Fischer, Pb(II) from Allied chemicals and Hg(II) from Mallinckrodt], tetramethyl ammonium nitrate (Johnson Matthey Electronics), methanol, tetramethyl ammonium hydroxide, nitric and hydrochloric acid (Aldrich) were used without further purification. Deionized distilled water was used for the potentiometric and solution calorimetric studies. All of the chemicals for the synthesis of macrocycles were purchased from the Aldrich Chemical Company. Molecular weights were determined by electron impact HRMS, and the data of elemental analysis of each macrocycle were obtained by Yamato CHN coder.

Preparation of L_1 (Cryptand 1,2B; 3,5-benzo-9,14,17-trioxa-1,7-diazabicyclo-(8,5,5) heptadecane) and L_2 (Cryptand 2,2B; 3,5-benzo-10,13,18,21-tetraoxa-1,7-diazabicyclo (8,5,5) eicosane). 1,4,10-Trioxa-7,13 diazacyclopentadecane (0.56 g, 2.58 mmol) or 1,4,10,13-Tetraoxa-7,16 diazacyclo-octadecane (0.65 g, 2.48 mmol) was stirred with 0.68 g (2.67 mmol) of α,α' -dibromo-*m*-Xylene in 15 ml of CH_3CN solution containing 15 g of Na_2CO_3 at room tempera-

ture and refluxed overnight. After being cooled, the reaction mixture was filtered and CH_2Cl_2 (50 ml) was added. The mixture was stirred and filtered. The filtrate was concentrated and the residue was chromatographed on alumina using $\text{THE}/\text{CH}_2\text{Cl}_2$ (1:1) as eluents to obtain 75-80% of L_1 and L_2 , respectively.

L_1 : $^1\text{H-NMR}$ δ 2.84 (m, 8H), 3.63 (m, 16H), 6.2-6.8 (m, 3H), 8.60 (s, 1H); $^{13}\text{C-NMR}$ δ 54.85, 58.62, 68.93, 70.06, 120.48, 125.62, 128.02, 140.35; Ms m/e 320, mp. 100°C

L_2 : $^1\text{H-NMR}$ δ 2.72 (m, 8H), 3.61 (m, 20H), 6.90-7.15 (m, 3H), 8.42 (s, 1H); $^{13}\text{C-NMR}$ δ 56.12, 59.64, 69.67, 70.60, 125.62, 127.24, 129.88, 142.07; Ms m/e 364, mp. 101°C

Preparation of L_3 (Cryptand 3,3B; 3,5-benzo-10,13,16,19,21,24,27-hexaoxa-1,7-diazabicyclo-(11,11,5) hexacosane). α,α' -diamino-*m*-Xylene (0.68 g, 2.67 mmol) was stirred with ditosyl ethers of glycol¹⁸ in 20 ml of CH_3CN containing 15 g of K_2CO_3 at room temperature and refluxed overnight. This mixture was treated in condition for preparation of L_2 .

L_3 : $^1\text{H-NMR}$ δ 2.65 (t, $J=6.3$ Hz, 8H), 3.60 (m, 28H), 7.1 (m, 3H), 7.9 (s, 1H); $^{13}\text{C-NMR}$ δ 55.24, 60.60, 70.44, 70.89, 71.20, 127.52, 127.72, 129.61, 141.14; mp. 104°C; MS m/e 452, Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{N}_2\text{O}_6$; C, 63.69; H, 8.90 Found: C, 63.48; H, 9.02

Preparation of L_4 (Cryptand [22'2]; 5,8,15,18,23,26-hexaoxa-1,12-diazabicyclo-(10,8,8) octacosane).

Table 1. Protonation and Stability Constants of Cation Complexes with Macrocycles at 25°C and $1=0.1$ mol. dm^{-3} (MeNNO_3) in Water-Methanol Media

| Cations | Mole-ratio ($L: \text{M}^{2+}$) | log K of complex with ligand | | | | Media | ΔH ($T\Delta S$) (Kcal/mol) | Methods |
|------------------|--------------------------------------|--------------------------------|-------------------|--------------------|----------------------|----------|--|---------|
| | | L_1 | L_2 | L_3 | L_4 | | | |
| H^{2+} | pK_1 | 8.69 | 10.39 | 11.52 | 9.69 | 50%-MeOH | | Pot. |
| | pK_2 | 5.54 | 5.64 | 5.83 | 7.40 | | | |
| Cd^{2+} | 1:1 | 2.26 | 6.52 | — | 4.26 | 50%-MeOH | -7.28 (-8.35) | Pot. |
| | | — | 5.48 | — | — | 20%-MeOH | | Pot. |
| | — | 6.08 | — | — | 50%-MeOH | Cal. | | |
| | 2:1 | 1.24 | 5.26 | — | — | 50%-MeOH | | Pot. |
| Pb^{2+} | 1:1 | — | 5.85 | 6.47 | 6.59 | 50%-MeOH | -11.9 (-12.8) | Pot. |
| | | — | 3.62 | 4.58 | — | 20%-MeOH | | Pot. |
| Hg^{2+} | 2:1 | 0.09 | 1.79 | — | — | 50%-MeOH | Pot. | |
| | 1:1 | — | 11.0 | 10.3 | 13.2 | 50%-MeOH | Pot. | |
| Ni^{2+} | 2:1 | 20.5 | — | — | — | 50%-MeOH | Pot. | |
| | 1:1 | 3.18 | 4.72 | — | 2.86 | 50%-MeOH | Pot. | |
| Zn^{2+} | 1:1 | 2.93 | 2.16 | — | — | 50%-MeOH | Pot. | |
| | Cryptand 22 | Cryptand 222 | Cryptand 221 | Cryptand 211 | Medium | Methods | | |
| Cd^{2+} | 5.13 | 7.10 | 10.0 ^a | <5.3 ^a | H_2O | pot | | |
| Pb^{2+} | 6.90 | 12.0 ^a | 15.1 ^a | 7.93 ^a | H_2O | pot | | |
| Hg^{2+} | 17.9 ^a | 18.2 ^b | 20.0 ^a | 15.9 ^a | H_2O | pot | | |
| Ni^{2+} | — | <2.50 ^b | 4.28 ^a | <4.50 ^a | H_2O | pot | | |
| Zn^{2+} | 3.19 | 2.48 ^a | 5.41 ^a | <5.30 | H_2O | pot | | |

^aReed M. Izatt, J. S. B. Bradshaw, S. A. Nielson, J. D. Lamb, and J. J. Christensen, Chem. Rev., **85**, 271-339 (1985).

^bG. Andereg, Helv. Chim. Acta, **58**, 1218 (1975).

1,10-diamino-4,7-dioxadecane needed for cryptand [22'2], L_4 , was prepared from ethane-1,2-diol after cyanoethylation and reduction with lithium aluminum hydride in THF⁷. A step-wise cyclocondensation of 1-chloro-8-iodo-3,6-dioxaoctane (3.50 mmol) and 1,10-diamino-4,7-dioxadecane (0.268 g, 1.52 mmol) in the presence of sodium carbonate in acetonitrile solvent gave cryptand [22'2], L_4 .

L_4 : ¹H-NMR δ 1.70 (m, 4H), 2.51 (t, $J=6.3$ Hz, 4H) 2.60 (m, 8H), 3.65 (m, 20H); ¹³C-NMR δ 24.2, 46.0, 48.3, 69.6, 70.3, 70.6; MS m/e 404, Anal. Calcd for $C_{20}H_{40}N_2O_6$: C, 59.44; H, 9.980, Found: C, 59.32; H, 10.01.

Potentiometric Measurements. Protonation and stability constants for the ligands were determined potentiometrically using an Orion-Ross double junction semimicro combination glass electrode. The semimicro potentiometric titrations were carried out in a sealed, thermostated vessel (5 ml, $25 \pm 0.1^\circ\text{C}$) under CO_2 free nitrogen atmosphere. During each titration run, the e.m.f. values under constant ionic strength were recorded as a function of amount of titrant added. Standard electrode potential, E° (320.2 mV) and the ion product of water at 0.1 M ionic strength, pH_w (13.70) were determined by titrating a HNO_3 solution to a standardized Me_4NOH solution. The protonation and stability constants (Table 1) were computed from data obtained by titrating acidified ligand solutions with Me_4NOH in the absence and presence, respectively, of the metal ion.

The ionic strength was maintained at 0.1 M with Me_4NNO_3 for all the titrations. The filling solution of the electrode was 0.8 M Me_4NNO_3 . Program SUPERQUAD⁸ was used for all the calculations.

Calorimetric Measurements. A Tronac Model 450 isoperibol titration calorimeter was used throughout. Enthalpies of protonation and metal ion binding for ligands were determined by a calorimetric titration technique described previously.⁹ Corresponding entropy values can be calculated according to the relation: $2.303 RT \Delta \log K = \Delta H - T \Delta S$. The ionic strength of 0.1 M was also maintained with Me_4NNO_3 for all the calorimetric titrations. Program REACTIONS¹⁰ was used for all the calculations of the calorimetric data.

NMR Measurements. ¹H and ¹³C-NMR spectra were measured on a varian Gemini 200 MHz spectrometer. The NMR solvent was in CD_3OD and the chemical shifts were referenced to Me_4Si .

Results and Discussion

The synthetic ligands can be regarded as tricyclic compounds. They can also be considered as derivatives of diaza-crown with an alkylene-ether chain linking two nitrogens. In ligands, L_1 - L_3 . The bridge consists of five atoms with its limited flexibility by the presence of a rigid benzene ring which shares three atoms with the bridge. The interatomic distance between two nitrogen atom is 6.7 \AA ¹¹ for L_2 ligand and the L_2 and L_3 may be shorter or longer than the L_4 . For L_4 , a more flexible bridge with ten atoms joined two nitrogen atoms, the N - N interatomic distance is 7.08 \AA ⁷ which is approximately 0.2 \AA longer than the 6.87 \AA for cryptand [222]¹¹.

The potentiometric titration-curves for the L_2 and its Hg^{2+} complex were given in Figure 2, and protonation and stability constants of several cation complexes with macrocycle, L_1 - L_4

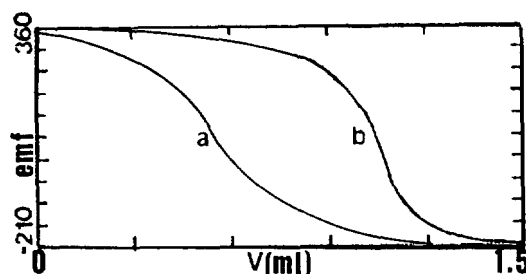


Figure 2. Potentiometric titration curves of macrocycle (L_2) (a) and its $\text{Hg}(\text{II})$ complex (b).

were also presented in Table 1 for comparison the synthetic ligands with regular cryptands.

The order of the basicity in Table 1 was $L_3 \geq L_4 > L_2 > L_1$ and then it is indicating that order of the basicities are increased regularly with increase in the cavity-sizes of macrocyclic ring. The basicity trends can be explained in terms of the degree of twistness and cavity-size of the macrocyclic ring¹². Hence, the twistness of tricyclic compounds were increased in order of $L_1 < L_2 < L_4 \leq L_3$. The changes of the stability constants of L_1 - L_4 complexes for the post transition metal ions were independent on the basicity. However, the order of the complex stabilities was $\text{Ni}^{2+} < \text{Zn}^{2+}$ for L_1 and L_2 , and $\text{Pb}^{2+} < \text{Cd}^{2+} < \text{Hg}^{2+}$ for L_1 - L_3 . Thus, the stabilities of the complexes were dependent on the cavity-size of the macrocycles because most of metal ions follow the size rule. The stabilities of the 18-crown-6 complexes containing soft cations such as Ag^+ , Tl^+ , Hg^{2+} and Pb^{2+} , also showed similar trend to follow this size rule¹³. Especially, the Hg^{2+} ion stability constants are higher than those of Cd^{2+} and Pb^{2+} ions because entropy effect is increased by forming the complexes. The same results were observed in metal complexes with other ligands¹⁴⁻¹⁵.

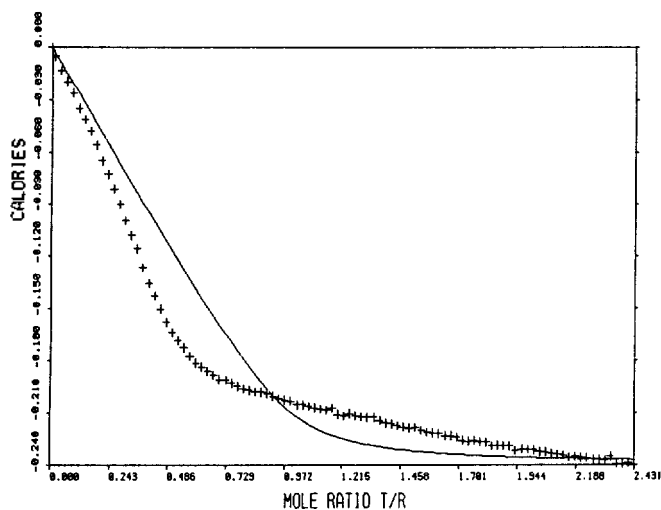
The stability constants for 1 : 1 cation-macrocycle complexes reveal that $\log K$ values for complexes with L_2 and L_3 were much smaller than those with the L_4 for all cations in this study. Ligand, L_2 , is similar to the cryptand 221 in configuration and number of donating atoms, but it is expected that cavity size of macrocyclic ring for L_2 is smaller than cryptand 221 because of benzene ring attached to the ligands. In this study, the $\log K$ values for $\text{Cd}(\text{II})$ and $\text{Zn}(\text{II})$ complexes with L_2 were larger than those with cryptand 22 because the flexibility of L_2 is higher than the cryptand 22 and 221. However, the stability constants of $\text{Pb}(\text{II})$ and $\text{Hg}(\text{II})$ complexes with L_2 were smaller than those with cryptand 22 and 221 because the cavity-size of L_2 is smaller than those of the cryptand 22 and 221. Thus, these results can be explained as ion-in-the hole model and the flexibility of macrocycles¹¹.

Frensdorf¹⁶ noted that $\log K$ values for the reaction of cyclic polyethers with metal cations are 10^3 - 10^4 larger in methanol than in water. The $\log K$ values listed in Table 2 was increased regularly with increase in weight percent of CH_3OH . The enhancement of stability in methanol is primarily an enthalpic effect¹⁷. The enthalpic stabilization is explained by the cation desolvation step in the solvent of lower dielectric constant. Generally, most of the complexes listed in Table 1 have 1 : 1 mole-ratio, except for Hg^{2+} - L_1 complex. On the other hand, stoichiometry of 2 : 1 (ligand: metal) for Hg^{2+} and Cd^{2+} complexes gives a sandwich type¹³. Thermo-

Table 2. ¹H-chemical shifts of macrocycles 1,2,3- and 4 affected by Cd²⁺ and Pb²⁺ ion^a

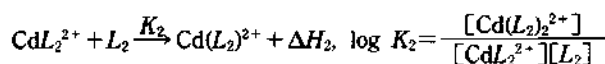
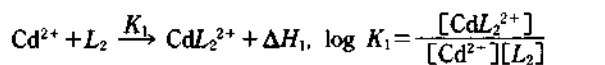
| Ligand Protons | L ₁ | | | L ₂ | | | L ₃ | | | L ₄ | | | |
|-------------------|----------------|----------------|----------------|---------------------|---------------------|---------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| | H _a | H _b | H _c | H _a | H _b | H _c | H _a | H _b | H _c | H _a | H _b | H _c | H _d |
| Ligand (ppm) | 2.84 | 3.63 | 4.60 | 2.72 | 3.61 | 4.40 | 2.65 | 3.60 | 4.90 | 1.70 | 2.51 | 2.60 | 3.65 |
| Comp. (ppm) | 2.86 | 3.68 | 4.63 | 2.78 | 3.76 | 4.52 | 2.69 | 3.71 | 4.99 | 1.75 | 2.62 | 2.63 | 3.77 |
| Shift (ppm) | 0.02 | 0.05 | 0.03 | 0.06 | 0.15 | 0.12 | 0.04 | 0.11 | 0.09 | 0.05 | 0.11 | 0.03 | 0.12 |
| | | | | (0.04) ^b | (0.13) ^b | (0.06) ^b | | | | | | | |

^a in ppm ^b data of Pb²⁺ ion. ^cH_a: NCH₂CH₂O, H_b: NCH₂, H_c: NCH₂σ for L₁, L₂ and L₃. ^dH_a: NCH₂CH₂CH₂O, H_b: NCH₂, H_c: NCH₂CH₂O, NCH₂CH₂O for L₄

**Figure 3.** Calorimetric titration curves of Cd(II) complex with L₂. [-; 1:1 and +; 2:1 ([L]: [Cd²⁺])mole-ratio]

dynamic parameters of the L₂-complex with Cd²⁺ which were obtained by using the computer program, REACTION indicated that log K and enthalpy of reaction are 6.08, -7.28 Kcal/mol (ΔH₁), and 4.78, -4.62 Kcal/mol (ΔH₂) for 1:1 or 2:1 mole-ratio, respectively.

The reaction of this complex is a stepwise type as follows:



Result for determination of equilibrium ratio of the metal ion to macrocyclic ligand, L₂, was given in Figure 3.

Generally, the ionic radius that matches best the radius of the cavity of the cryptand will form the most stable complex. The correspondance between cavity size and complex stability is more pronounced with the cryptands than coronands. This correspondance between log K values and match of macrocycle cavity and cation diameters was also found for this study. Log K values of post transition metal complexes for L₁-L₄ cryptands are larger than those of alkali and alkaline earth-cryptates⁷. The ion-dipole interactions with post transition metal ions should be favorable for the combination of the soft donor sites of N and S atoms in macrocycles. The stability of the complexes formed by cryp-

tands L₁-L₄. Shows the cryptate effect. The cavity sizes of L₁-L₃ are smaller than the regular cryptands because of benzene molecule. Thus, it is apparent from the data in Table 1 that the new cryptands (L₁-L₃) form much weaker complexes with all the cations studied than original cryptands (cryptands 22, 222, 221, 211) except for L₂ which formed a stronger complex with Cd²⁺ than cryptand 22. Because of small cavity size of L₂ as compared to those of cryptand 211 and 22, respectively, it was expected that the L₂ should form more stable complex with smaller cations such as Cd²⁺ ion. However, Ligands L₂-L₄ have moderate interactions with Cd²⁺, Pb²⁺ and Hg²⁺ ions in aqueous-methanol solutions. Cd²⁺ and Pb²⁺ ions have no significant interaction with L₁, but Hg²⁺ complex has the strongest stability constant as 2:1 ([L₁]: [Hg²⁺]) mole-ratio. The stability constants of the post transition metal complexes with L₄ were smaller than those with cryptand 222 because the cavity size of L₄ is increased by incorporating two more methylene unit into the regular cryptand 222. It is interesting that L₂ exhibits selectivity for Cd²⁺ over Pb²⁺ ion and other transition metal ions. In case of the L₃ and L₄ complexes, the post transition metal ions were expected to be much smaller than the cavity, while in case of complexes with L₁, Cd²⁺ ion was expected with similar size for the cavity, and in case of complexes with L₁, the post transition metal ions were expected to be much larger than the cavity size. Furthermore, the size of Hg²⁺ ion was much larger than the ligand cavity. Thus, Hg²⁺ ion forms complex with L₁ out of the cavity of the macrocycle and the effect of macrocyclic ring size becomes more important.

The complex solutions for determination of proton chemical shifts were prepared by mixing the macrocycles and excess the post transition metal ions, Cd²⁺ and Pb²⁺, in methanol-d₄ for 24-hours.

The proton chemical shifts for Cd²⁺ and Pb²⁺ complexes with L₁, L₂, L₃, and L₄ and the free ligands were listed in Table 2.

All of the proton resonance lines for the OCH₂ group were nearly constant but those for NCH₂ and NCH₂CH₂O groups adjacent to the nitrogen donor atoms were shifted to downfield direction for all the complexes as compared with the free ligands. In addition, chemical shift-values for the cadmium(II) complexes were also increased with the order of L₁<L₃<L₄<L₂. The proton resonance lines were shifted to downfield because the electronegativity of the donor atoms were increased due to the interaction of the post transition metal ion and donor atoms. These proton signals were well

Table 3. The ^{13}C -chemical shifts of $L_2\text{-Cd}^{2+}$ and Pb^{2+} ion complexes

| Complex | Resonance line | | | | | | | |
|------------------|-------------------|----------------|---------------------------|----------------|------------|--------|--------|--------|
| | ρCH_2 | NCH_2 | NCH_2CH_2 | OCH_2 | Aromatic C | | | |
| Ligand(ppm) | 56.12 | 59.64 | 69.67 | 70.60 | 125.62 | 127.24 | 129.88 | 142.07 |
| Cd^{2+} | 54.36 | 57.16 | 68.92 | 69.92 | 123.68 | 125.18 | 126.49 | 143.52 |
| Pb^{2+} | 54.76 | 58.02 | 69.06 | 70.21 | 123.92 | 126.02 | 125.71 | 143.71 |

separated in nice doublet or triplet in the range of 2.69-4.99 ppm for the methylene signals of the Cd^{2+} complexes with $L_1\text{-}L_3$ ligands and 1.75-3.77 ppm for the methylene signals of the complex with L_4 ligand.

The ^1H -NMR spectra of the samples containing $L_1\text{-}L_3$ and Cd^{2+} and Pb^{2+} ions showed that the aromatic signals of the macrocycles were a doublet and triplet. Both of signals were well resolved in the range of 6.90-7.20 ppm for L_2 and these were well separated from benzene group of free ligands. Thus, the formation of the post transition metal complexes with these macrocycles was mainly due to the interaction of the metal ions and the nitrogen donor atoms rather than that of the oxygen donor atoms, and the interaction of the metals and nitrogen atoms leads to an enhancement of the metal ion affinity, and the aromatic signals of macrocycles were used as a probe for monitoring the complexation. The ^{13}C -NMR chemical shifts for complexes with L_2 and the free ligand were listed in Table 3. These signals were mostly shifted to the direction of high magnetic field, whereas the signals of some carbon atoms of the benzene ring were shifted to down magnetic field because of the perturbation of ring current of benzene-molecule that is due to the interaction of the complex ion and counter anion.

Therefore, ^1H and ^{13}C -NMR studies indicated that the nitrogen atoms of cryptates have greater affinity to metal ions than the oxygen atoms, and that the planarities of the macrocyclic ring are lost by complexation with the post transition metal ions.

Acknowledgement. This Paper was Supported NON DIRECTED RESEARCH FUND, Korea Research Foundation, 1992.

References

1. Y. Inoue and G. W. Gokel, 'Cation Binding by Macrocycles', 1p, Dekker, New York, NY, U.S.A. (1991).
2. A. Bencini, A. Bianchi, E. Garcia-Espana, M. Giusti, S. Mangani, M. Micheloni, P. Orioli, and P. Paoletti, *Inorg. Chem.*, **26**, 1243 (1987).
3. M. Micheloni, P. Paoletti, and Avacca, *J. Chem. Soc. Perkin Trans.*, **2**, 945 (1978).
4. M. Bartolini, A. Bianchi, M. Micheloni, and P. Paoletti, *J. Chem. Soc., Perkin Trans.*, **2**, 1345 (1982).
5. H. Y. An, J. S. Bradshaw, and R. M. Izatt, *Chem. Rev.*, **92** (1992).
6. J. S. Bradshaw, H-Y An, K. E. Krakowiak, G. Wu, and R. M. Izatt, *Tetrahedron*, **46**, 6985 (1990).
7. R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, and J. J. Christensen, *Chem. Rev.*, **85**, 271 (1985).
8. Peter Grans, *J. Chem. Soc. Dalton Trans.*, 1195 (1985).
9. R. M. Izatt, J. D. Lamb, N. E. Izatt, B. E. Jr. Rossiter, J. J. Christensen, and B. H. Haymore, *J. Am. Chem. Soc.*, **101**, 6273 (1979).
10. R. D. Hancock and A. E. Martell, *Chem. Rev.*, **89**, 1875 (1989).
11. E. Krakowiak, J. S. Bradshaw, N. K. Dalley, C. Y. Zhu, Guoliang Yi, J. C. Curtis, Du Li, and R. M. Izatt, *J. Org. Chem.*, **57**, 3166 (1992).
12. B. Metz, D. Moras, and R. Weiss, *J. Chem. Soc., Perkin Trans. II*, 423 (1976).
13. M. Kodama and E. Kimura, *J. Chem. Soc. Dalton Trans.*, 2335 (1976).
14. M. Kodama and E. Kimura, *J. Chem. Soc. Dalton Trans.*, 2356 (1976).
15. G. W. Gokel, D. M. Goli, C. Miganiti, and L. Echegoyen, *J. Am. Chem. Soc.*, **105**, 6786 (1983).
16. H. K. Frensdorf, *J. Am. Chem. Soc.*, **93**, 2967 (1971).
17. P. Gans, A. Sebatini, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1195 (1985).
18. M. Pietraskiewicz, R. Gassiorowski, and J. Kozbial, *J. Incl. Phenom.*, **7**, 309 (1989).