

CHAPTER III

RESULTS AND DISCUSSION

3.1 Spectral variations of systems studied

UV spectra of free ligands studied exhibited an intense band at the vicinity of 280 nm, possibly an absorption peak of phenol groups [36]. This absorbance range may be used as a criterion for complex formation because strong complexation usually results in large changes in both absorption position and intensity [36]. Some of spectral changes obtained upon addition of metal solution are depicted in Figures 3.1 to 3.3.

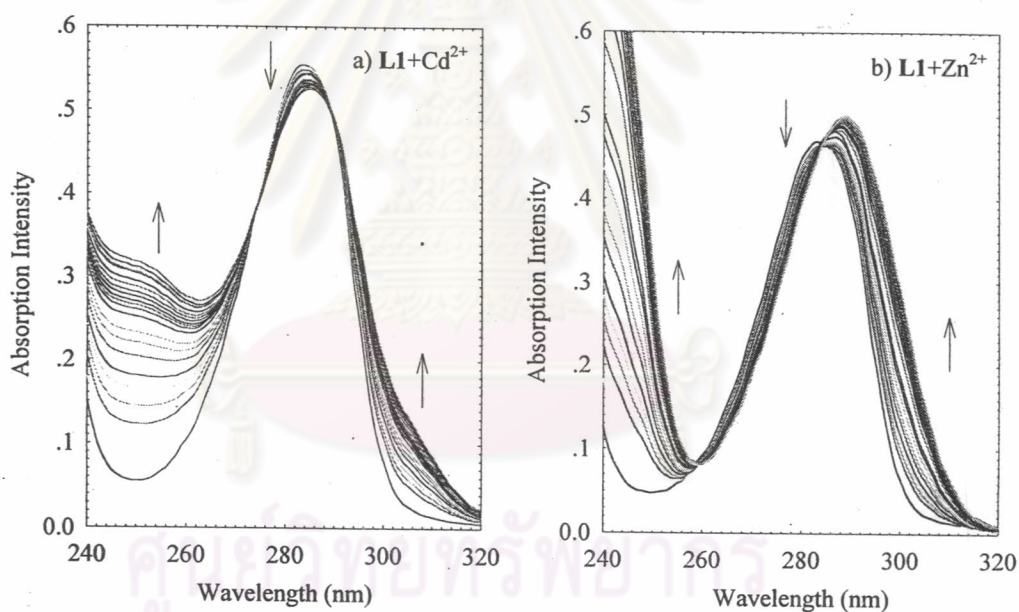


Figure 3.1 Spectral changes in the UV absorption of L1 ($C_L \approx 1 \times 10^{-4}$ M) in MeOH ($I = 0.01$ M Et₄NCl) upon addition of a: Cd²⁺ ($0 \leq C_M/C_L \leq 10$); b: Zn²⁺ ($0 \leq C_M/C_L \leq 255$)

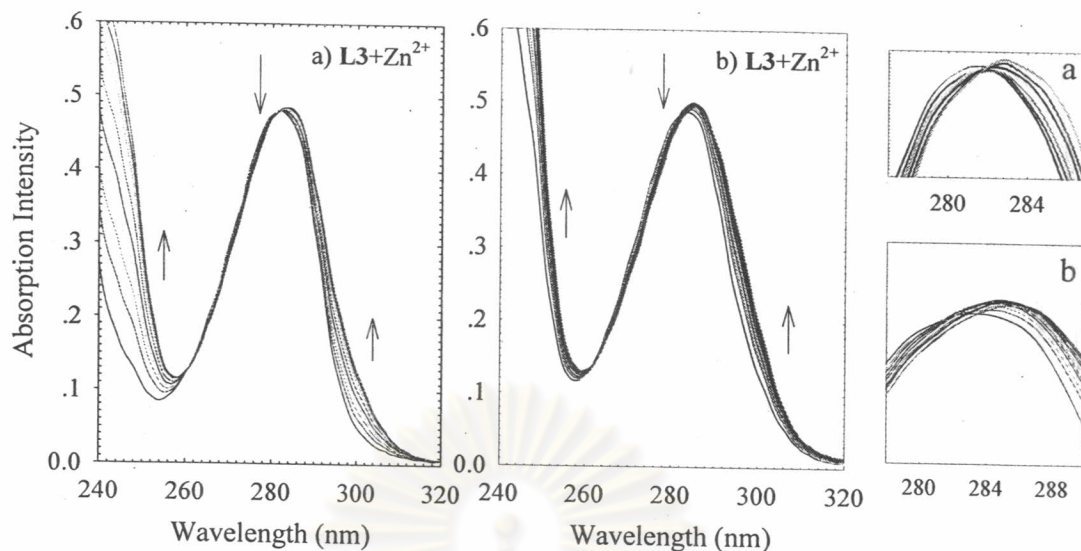


Figure 3.2 Spectral changes in the UV absorption of L3 ($C_L \approx 1 \times 10^{-4}$ M) upon addition of Zn²⁺ in MeOH ($I = 0.01$ M Et₄NCl) a: $0 \leq C_M/C_L \leq 7.3$; b: $7.3 < C_M/C_L \leq 220.3$

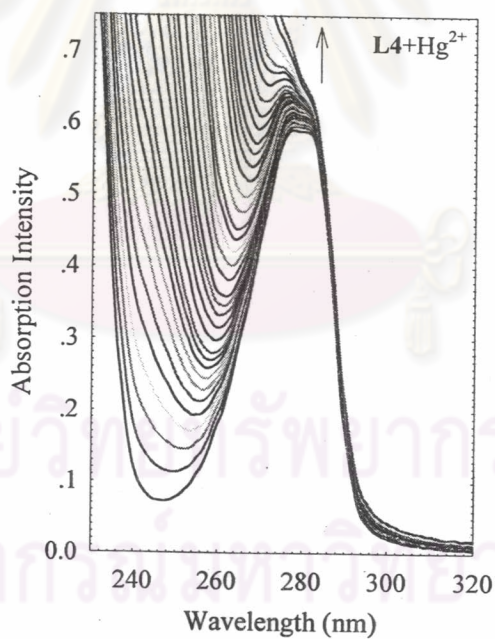


Figure 3.3 Spectral changes in the UV absorption of L4 ($C_L \approx 1 \times 10^{-4}$ M) upon addition of Hg²⁺ in MeOH ($I = 0.01$ M Et₄NCl): $0 \leq C_M/C_L \leq 16$

In complexation study using UV spectrophotometric titration, spectral changes are employed for monitoring complex formation. As seen in Figures 3.1 and 3.2, the successive addition of metal causes a bathochromic shift, i.e. λ_{\max} shifted to higher wavelength. The only exception is Hg^{2+} complex of L4 where a hypsochromic shift was observed as shown in Figure 3.3. Both hyperchromic and hypochromic shifts were found depending on the systems studied. A number of isosbestic point(s), often taken as criteria for the existence of at least two interconvertible absorbing species, were found in the complexation of Zn^{2+} and Cd^{2+} as can be seen in Figures 3.1 and 3.2.

When UV spectrophotometric titration is used for monitoring complexation, molar absorptivities of all absorbing species must be refined in order to obtain reliable stability constants. In this research, stability constants of complexes could be refined satisfactorily and trustworthily, excluding those of Cu^{2+} complexes owing to high UV radiation absorbability of metal ion itself as shown in Figure 3.4. In the experiments of lead ion, the undesired precipitate between Pb^{2+} and Cl^- (from supporting electrolyte Et_4NCl) was formed in the spectrophotometric cell. Thus stability constants of Pb^{2+} complexes using Et_4NCl to maintain ionic strength were unable to be exactly evaluated. To obtain stability constants of Pb^{2+} complexes, ammonium salts was changed from Et_4NCl to Bu_4NNO_3 . With a new choice of supporting electrolyte, the stability evaluation of Pb^{2+} complexes could be achieved.

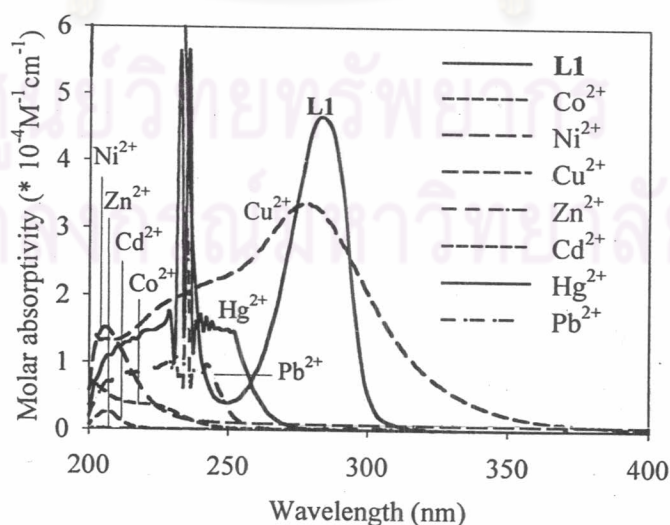


Figure 3.4 Molar absorptivities of L1 and metal ions studied in MeOH

3.2 Nature of complexes

Experimental results showed only ML formation in most of the systems studied, with the exception of Co^{2+} and L4, and Cd^{2+} and L6 where only ML_2 complexes were found. Besides commonly formed ML complex, the ML_2 complex was also found in the system of Pb^{2+} . The other binuclear complex M_2L was also formed in the systems of Zn^{2+} with L1, L3 and L4.

3.3 Stability constants

All stability constants of complexes refined using program Sirko [22] are tabulated in Table 3.1.

Table 3.1 Stability constants ($\log \beta$)^a of complexes between diazacrown ethers and metal ions in methanol (T = 25 °C, I = 0.01 M Et_4NCl , except stated otherwise)

metal	model	L1	L2	L3	L4	L5	L6
Co^{2+}	ML	4.01 (0.05)	5.05 (0.05)	5.35 (0.01)		4.74 (0.04)	4.44 (0.01)
	ML_2				9.24 (0.23)		
Ni^{2+}	ML	3.75 (0.01)	4.22 (0.03)	3.85 (0.02)	3.76 (0.04)	3.86 (0.06)	4.67 (0.04)
Zn^{2+}	ML	3.44 (0.06)	3.08 (0.03)	3.51 (0.02)	3.78 (0.04)	3.22 (0.02)	3.34 (0.03)
	M_2L	5.60 (0.01)		5.38 (0.08)	6.35 (0.06)		
Cd^{2+}	ML	3.82 (0.01)	4.11 (0.01)	3.79 (0.03)	4.68 (0.04)	4.26 (0.04)	
	ML_2						8.08 (0.05)
Hg^{2+}	ML	4.41 (0.01)	4.14 (0.02)	3.45 (0.01)	3.62 (0.02)	4.26 (0.01)	3.40 (0.01)
Pb^{2+b}	ML	≥ 7	≥ 7	≥ 7	≥ 7	≥ 7	6.17 (0.01)
	ML_2	≥ 11.0	≥ 12.6	≥ 13.0	≥ 12.5	≥ 12.1	12.05 (0.09)

^a mean values of at least two independent determinations, with standard deviation σ_{n-1} on the mean in parentheses

^b I = 0.01 M Bu_4NNO_3

As can be seen in Table 3.1, there are two major factors affecting stability constants of complexes studied, i.e. an increasing number of carbon atoms in side arms, and a type of metal ion. From Table 3.1, it may be noted that, in general, the longer the alkyl substituent is, the more stable the complex.

3.3.1 Stability constants in terms of ligands

It was obviously shown that complex stability had been influenced by side arms of the crown ethers. In order to make the discussion easier, the ligands will be divided into two categories:

- a) ligands with linear hydrocarbon substituents **L1-L4**
- b) ligands with branch hydrocarbon substituents **L5 and L6**

3.3.1.1 Ligands with linear hydrocarbon substituents

Hydrocarbon chains are incorporated to the ligands at *para* position of phenol groups except **L4** at *meta* position. These chains can increase electron density to hydroxy functional groups of phenols through bonds and space, which is referred to as an *inductive effect*. Electron induced from alkyl substituents to hydroxy groups for **L1**, for example, is illustrated in Figure 3.5. In addition, substituents incorporated into macrocyclic flexible ring lead to its rigidity and may alter both macrocycle binding strength and selectivity [37]. Stability constants of complexes as a function of number of carbon atoms are shown in Figures 3.6, stability constants of Co^{2+} and Pb^{2+} being omitted. Note that **L4** could not be compared to the other ligands because of the different position of alkyl attachment.

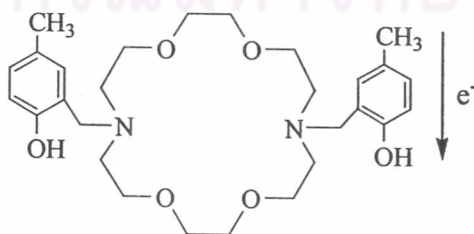


Figure 3.5 Electron induced from alkyl substituents to hydroxy groups for **L1**

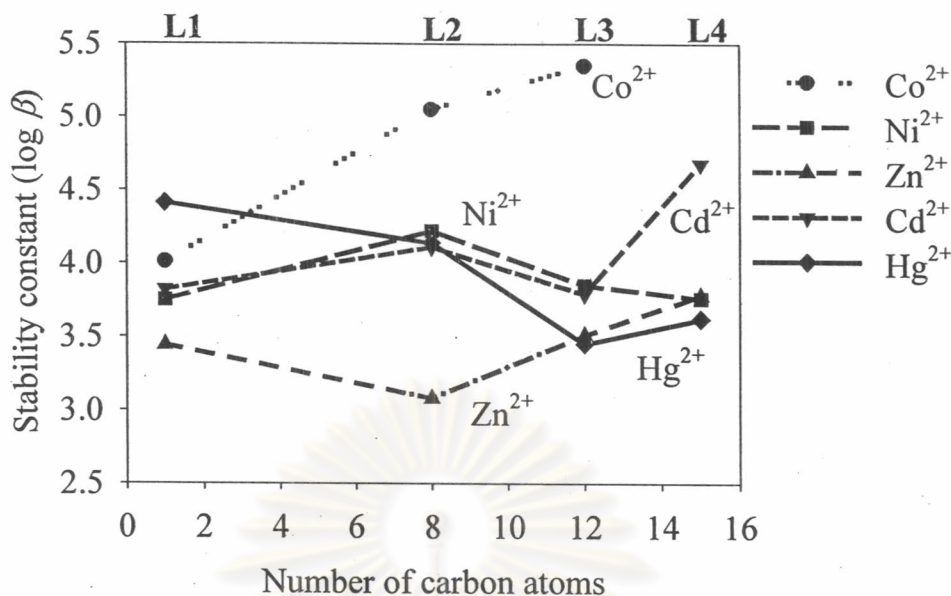


Figure 3.6 Stability constants ($\log \beta_{ML}$) of complexes studied as a function of number of carbon atoms (linear chain)

The trend in stability constants of Co^{2+} complexes is perfectly matched with the general trend, i.e. $\log \beta_{ML}$ increases along with the length of alkyl chain; possibly because Co^{2+} is small-sized and may be tetrahedrally bound to the ligands, which is a preferred geometry for Co^{2+} [38]. For ML_2 complex of Co^{2+} with **L4**, it is presumed that **L4** may be unable to arrange themselves to wrap around Co^{2+} due to a steric hindrance caused from the longest chains among ligands studied at *m*-position to OH group of phenols.

It is known that Ni^{2+} possessing 8 d-electrons preferably forms square planar complex; however, natural binding sites of crown ethers, controlled by the strain of macrocyclic ring and their side arms, cannot be easily arranged into the square planar geometry. Thus, Ni^{2+} complexes are usually less stable than are Co^{2+} complexes. The trend of stability order of Ni^{2+} complexes is different from that of Co^{2+} though, i.e. highest value of $\log \beta_{ML}$ comes from **L2** system. It is possible that **L2** could provide the square planar geometry for Ni^{2+} because of the ligand's low flexibility. The stability constants refined have revealed that the complexation of small-sized transition metal ions (i.e. 0.69 Å for Ni^{2+} , and 0.75 Å for Co^{2+} , based on 6 coordination sites [17]) is slightly affected by a hindrance from hydrocarbon chains. It

may be mentioned that a stability of transition metal complexes relies on ligand's reorganization to provide appropriate geometry for metal ion.

In the case of Zn^{2+} complexes, the stability trend for ML formation is congruent with the general trend. However, this cation formed both ML mononuclear and M_2L binuclear complexes in the same system. One exception is **L2** where only ML was found. Furthermore, this ligand formed the least stable mononuclear complex with Zn^{2+} among ligands studied. For binuclear M_2L formation, **L4** could take up a second metal ion more easily than could other ligands, as its stepwise stability constant $\log K_{M_2L} (= \log \beta_{M_2L} - \log \beta_{ML})$ of 2.57 is the highest among ligands studied. A proposed M_2L binding mode imitating binuclear complex $[Cu_2(\mathbf{16-2H})]^{2+}$ (**16** = N,N'-bis(2-salicylaldiminobenzyl)-4,13-diaza-18-crown-6) is illustrated in Figures 3.7 and different UV absorbabilities of ML and M_2L complexes of Zn^{2+} and **L1**, calculated from stability constants of this complex, are shown by their molar absorptivities as given in Figure 3.8.

For a given ligand, the complex stability order of the first row transition metal is generally: $Zn^{2+} < Ni^{2+} < Co^{2+}$. This order is identical to the stability order for the complexations of these metal ions with the parent crown ether (1,10-diaza 18-crown-6) obtained by potentiometry [40]. Compared to similar-structured ligand **15** (*o*-chlorophenol-4,13-diaza-18-crown-6 as shown in page nine), the stability constants of Zn^{2+} and Co^{2+} formed with **15** are contrast to the aforementioned order: $Zn^{2+} > Co^{2+}$, no evaluation for Ni^{2+} [16]. This is because the Cl^- substituent groups in **15** can induce electron density from phenol groups to themselves. This occurrence is a strong support for intramolecular hydrogen bonding within the ligand and may decrease a role of N bridgeheads in covalent contributions toward Co^{2+} .

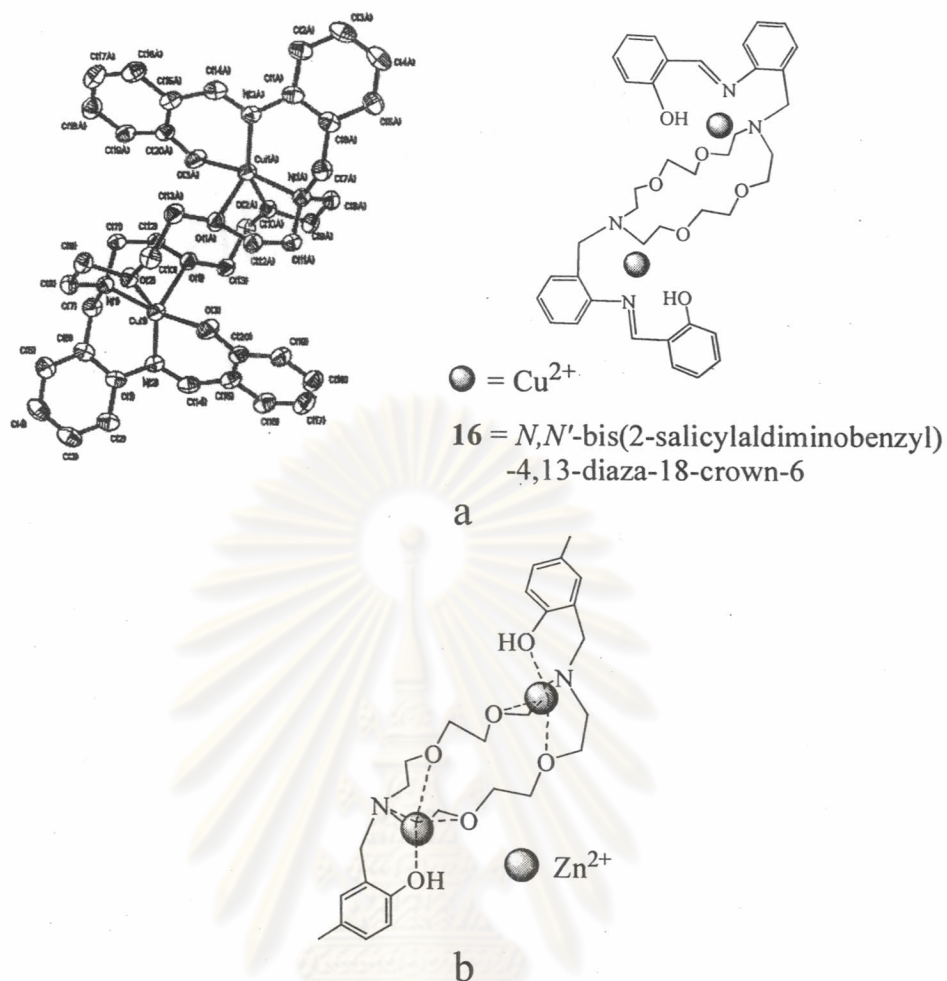


Figure 3.7 a: X-ray crystal structure of $[\text{Cu}_2(\mathbf{16}\text{-2H})]^{2+}$ [39], b: proposed binding mode for M_2L complex of $[\text{Zn}^{2+}\mathbf{L1}]$

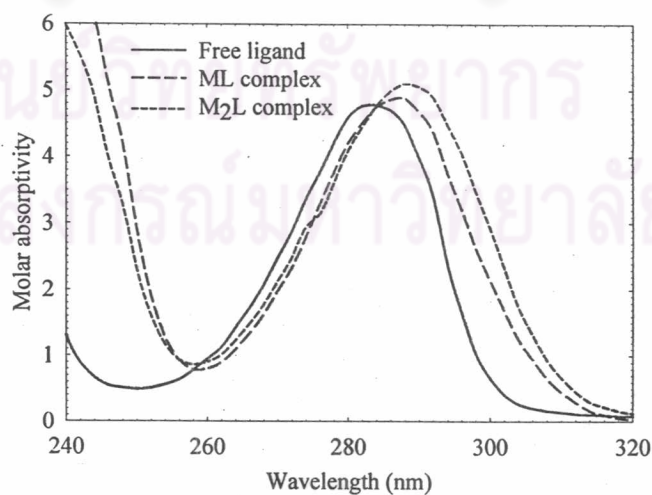


Figure 3.8 Molar absorptivities of $\mathbf{L1}$ and its complex with Zn^{2+}

Regarding Cd^{2+} complexes, the stability trend of this system is matched with the general trend, except Cd^{2+} complex of **L3**, possibly due to high rigidity and low reorganizability of this ligand. In the case of the largest-sized ion in IIB group Hg^{2+} , the least steric ligand **L1** formed most stable complex with Hg^{2+} among ligands studied ($\log \beta_{\text{ML}} = 4.41$). This might be because **L1** can arrange itself to provide appropriate binding cavity for Hg^{2+} more easily than can other ligands. The results have shown that the longer the substituent is, the less stable Hg^{2+} complex is observed. This indicates that an increase in length of ligand's side arms causing low reorganizability leads to less stable complex. Remarkably, Hg^{2+} complex of **L4** ($\log \beta_{\text{ML}} = 3.62$) is slightly more stable than is that of **L3** ($\log \beta_{\text{ML}} = 3.45$). It is suggested that **L4** might have less degree of ligand solvation than does **L3**, due to its longest side arms on *meta* position of the phenols.

Every ligand formed both ML_2 and ML complexes with Pb^{2+} , the largest metal ion studied, with $\log \beta_{\text{ML}_2}$ by **L1** being the least and that by **L2**, **L3**, and **L4** being comparable. Noteworthily, all of ligands formed very strong ML complexes with Pb^{2+} that the exact stability constants cannot be reliably reported and only the lower limit of $\log \beta$ by UV-Vis spectrophotometry is given. This is in accordance with earlier studies that Pb^{2+} is prone to form very stable complex with diazacrown ether derivatives such as diaza-18-crown-6 ($\log \beta_{\text{ML}} = 6.71$, evaluated by potentiometric titration) [41], 2-[16-(2-hydroxy-2-phenylethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecanyl]-1-phenyl-1-ethanol ($\log \beta_{\text{ML}} > 7.52$, evaluated by potentiometric titration) [41], 1,10-dibenzyl-1,10-diaza-18-crown-6 [42], *N,N'*-bis(2-aminobenzyl)-4,13-diaza-18-crown-6 ($\log \beta_{\text{ML}} = 7.7$, evaluated by UV-Vis spectrophotometric titration) [43], and *N,N'*-bis[(2-salicylaldimino)benzyl]-4,13-diaza-18-crown-6 ($\log \beta [\text{Pb}(\text{L-2H})_{\text{ML}}] = 7.2$, evaluated by UV-Vis spectrophotometric titration)[43]. Although $\log \beta_{\text{ML}_2}$ values do not allow the comparison of the affinity of ligands studied toward Pb^{2+} , it could be seen from the highest value of stepwise stability constant $\log K_{\text{ML} \leftarrow \text{ML}_2}$ of 2.98 for **L1** that the least steric ligand could form ML complex more readily than other ligands. Note that $\log K_{\text{ML} \leftarrow \text{ML}_2}$ can be calculated from the expression: $\log K_{\text{ML} \leftarrow \text{ML}_2} = 2 \log \beta_{\text{ML}} - \log \beta_{\text{ML}_2}$, and the values of $\log K_{\text{ML} \leftarrow \text{ML}_2}$ for **L1**, **L2**, **L3**, and **L4** are 2.98, 1.4, 1.0 and 1.5, respectively.

3.3.1.2 Ligands with branch hydrocarbon substituents

The experimental results have demonstrated that side arms of **L5** and **L6** affect stability constants as illustrated in Figure 3.9 (Cd^{2+} complex of **L6** being omitted due to ML_2 complex formation).

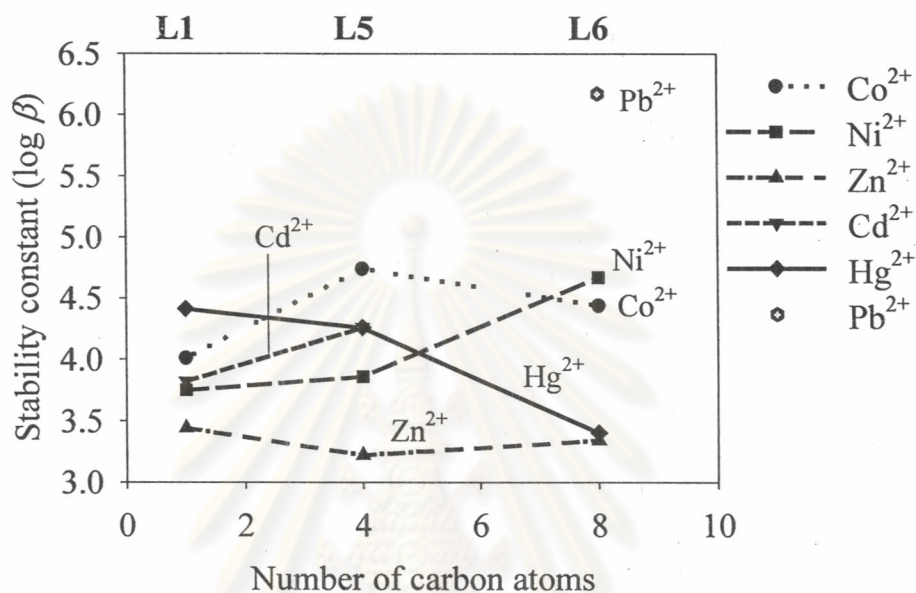


Figure 3.9 Stability constants ($\log \beta_{\text{ML}}$) as a function of number of carbon atoms (**L1**, **L5**, and **L6**)

Since Co^{2+} and Ni^{2+} are classified as transition metal ions, the main factor having an effect on their complexation is differences in their preferred coordination geometries. In this research, Co^{2+} generally formed more stable complexes than Ni^{2+} did. This is because an intrinsic binding mode of crown ether, controlled by a strain of macrocyclic ring and its side arms, is likely to be more appropriate for the former than for the latter. Nevertheless, there is the exception in the case of **L6**, which has slightly higher affinity for Ni^{2+} ($\log \beta_{\text{ML}} = 4.67$) than for Co^{2+} ($\log \beta_{\text{ML}} = 4.44$) as shown in Figure 3.9. Due to very steric hindrance, side arms of **L6** should arrange themselves as remotely from each other as possible so as to minimize structure's strain; causing low reorganizability. Consequently, binding sites of **L6** might provide square planar complex for Ni^{2+} , its preferred stereochemistry, as proposed in Figure

3.10, the Ni—N being shorter than Ni—O in consequence of a preference between transition metal ions and soft donor atoms.

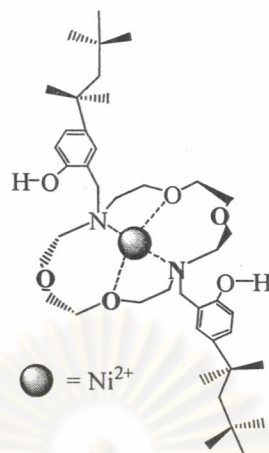


Figure 3.10 Proposed binding mode of Ni²⁺ complex of L6

The refinement has revealed that stability constant of Zn²⁺ with L6 ($\log \beta_{ML} = 3.34$) is very close to that with L5 ($\log \beta_{ML} = 3.22$). This means that bulky side arms affect complexation of Zn²⁺ only slightly. For this case, the substituents of the ligands might play a role in an arrangement of the ligand's binding sites so as to obtain appropriate and stable geometry for Zn²⁺ and in shielding Zn²⁺ from the solvation.

Because of differences in their side arms, L5 and L6 formed complexes with Cd²⁺ differently: ML for L5 and ML₂ for L6. Regarding Hg²⁺, the results have shown that the more steric the ligand is, the less stable Hg²⁺ complex is obtained ($\log \beta_{ML} = 3.46$ for L6 compared with 4.26 for L5). Lastly, Pb²⁺ complex of L6 is the only system where stability constant can be reliably reported. The fact that the stability of this complex is the least among Pb²⁺ complexes in this study ($\log \beta_{ML} = 6.17$) shows that the complexation is affected by ligand's bulkiness, notably for large metal ions. It should be noted that complexation between L6 and Pb²⁺ is still much stronger than other systems.

3.3.1.3 Comparison between ligands being equal in number of carbon atoms in substituents

Even if substituents of **L2** and **L6** are considered as *isomer*, both ligands do not have similar affinity for metals studied as shown in Figure 3.11 ($\log \beta_{ML}$ of $[\text{Pb}^{2+}\text{L2}]$ and $[\text{Cd}^{2+}\text{L6}]$ being omitted). Due to appropriate geometry caused by bulky substituents, **L6** has slightly higher affinity for Ni^{2+} ($\log \beta_{ML} = 4.67$) than for Co^{2+} ($\log \beta_{ML} = 4.44$). Contrastingly, **L2** has greater affinity for Co^{2+} ($\log \beta_{ML} = 5.05$) than for Ni^{2+} ($\log \beta_{ML} = 4.22$).

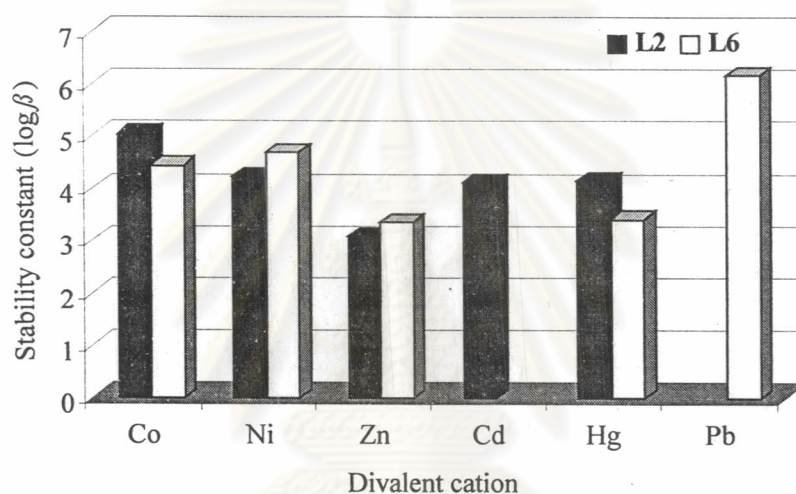


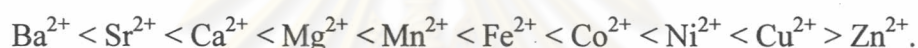
Figure 3.11 Stability constants ($\log \beta_{ML}$) of **L2** and **L6** with different metal ions

In the case of Zn^{2+} , its complex with **L6** ($\log \beta_{ML} = 3.34$) is slightly more stable than is that with **L2** ($\log \beta_{ML} = 3.08$). It is surmised that **L6** can exclude the presence of anion and solvent from the solvation sphere of the cation more effectively than **L2** can. Hg^{2+} complex of **L6** ($\log \beta_{ML} = 3.40$) is less stable than is that of **L2** ($\log \beta_{ML} = 4.14$) because of steric hindrance. This shows that Hg^{2+} and Zn^{2+} complexes display the contrasting trend of their stability constants due to different ionic sizes. Even though the side arms of ligands **L2** and **L6** are isomeric, Cd^{2+} complexes have different stoichiometries (ML complex for **L2** and ML_2 complex for **L6**). It may be inadequate to elucidate these phenomena only by the steric hindrance of the ligands, because a larger-sized metal Hg^{2+} (approximately 1.02 Å, [17]) formed just ML complex with **L6**, but a smaller-sized metal Cd^{2+} (approximately 0.95 Å,

[17]) skeptically formed ML_2 complex. This may be attributed to very low reorganizability of **L6**. Although Cd^{2+} and Hg^{2+} prefer nitrogen atoms rather than oxygen atoms [44], Cd^{2+} might bind oxygen atoms in crown ether rings more strongly than Hg^{2+} might, due to the polarizability order of IIB metal: $Zn^{2+} < Cd^{2+} < Hg^{2+}$ [17].

3.3.2 Stability constants in terms of metal ions

The seven metal ions studied in this research, i.e. Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , and Pb^{2+} , can be classified into two categories: a) the first row transition metal ions, i.e. Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} ; b) heavy metal ions, i.e. Cd^{2+} , Hg^{2+} , and Pb^{2+} . In complexation of alkaline earth and the first row d metal ions, the order of their stability is summarized by the Irving-Williams series [45]:



This order is relatively insensitive to the choice of open-chained ligands and evaluated by octahedral geometry complexation. An increase in stability usually progresses from metal ions of large radius to those of small radius, suggesting that the Irving-Williams series reflect electrostatic effect [45].

In this study, Co^{2+} generally formed the most stable complexes among metal ions studied. For a given ligand, the stability order of 1st row transition metal complexes is: $Zn^{2+} < Ni^{2+} < Co^{2+}$, which is different from the Irving-Williams series. This is because common binding modes of crown ethers are not octahedral stereochemistry and crown ethers are less flexible than are open-chained ligands. It should be mentioned, nevertheless, that even if the reliable stability constants for Cu^{2+} systems could not be obtained, there are evidences indicating that the complex formation of Cu^{2+} exists. First, the experimental absorption being different from the combination of absorptions of ligand and Cu^{2+} is found. This difference is assumed to be caused by their complexation, for example, in the complexation of **L6** with Cu^{2+} as illustrated in Figure 3.12. Second, a crystal structure of **L1**+ $Cu(NO_3)_2$ obtained by Ma et al. [46], shown in Figure 3.13, proves that **L1** can effectively bind Cu^{2+} .

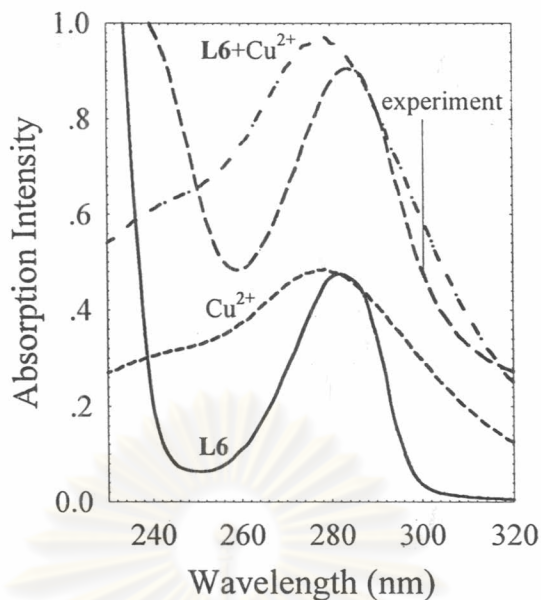


Figure 3.12 Spectral changes in the UV absorption of L6 ($C_L \approx 1 \times 10^{-4}$ M) upon addition of Cu^{2+} in MeOH ($C_M / C_L \approx 1$)

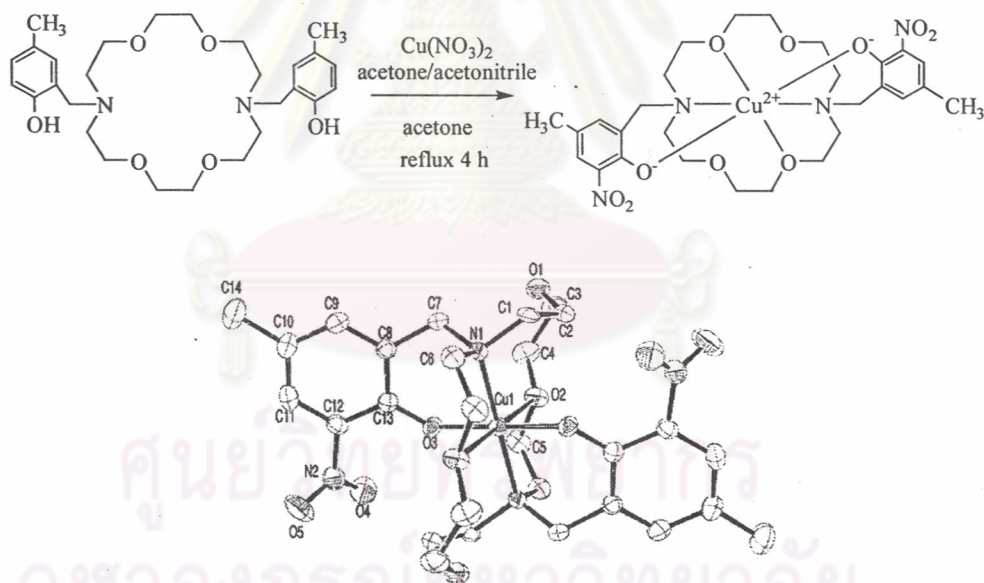


Figure 3.13 X-ray crystal structure of $[\text{CuL1}]$ showing the complex with the atom numbering scheme. The displacement ellipsoids are drawn at 50% probability level [45].

Since UV-Vis spectrophotometry cannot give the values of enthalpy and entropy; the size, preferred geometry, and type of bonding of metal ions are important factors that contribute to the stability of metal complexes studied.

The size of six metals studied is compared in Figure 3.14 (1 cm = 0.75 Å).

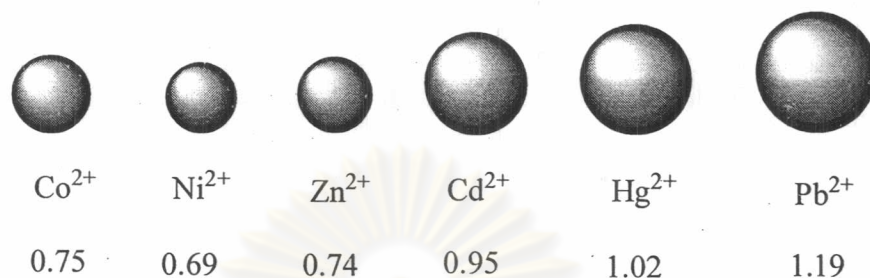


Figure 3.14 Ionic radius (Å) of metal ions studied [17]; Co²⁺, Ni²⁺, Pb²⁺ (effective ionic radius, 6 coordinate), Zn²⁺, Cd²⁺, Hg²⁺ (effective ionic radius, no reported coordination number)

The size of the first row transition metal ions studied is practically identical, but their stability constants are different. This may be due to a difference in a preferred geometry of each metal ion. In this research, Co²⁺ generally formed higher stable complexes than did Ni²⁺ and Zn²⁺, possibly because ligands studied can arrange themselves to provide more suitable geometries for Co²⁺ than for Ni²⁺ and Zn²⁺.

Regarding IIB metal ions, the stability order for the smallest ligand L1 is: Zn²⁺ < Cd²⁺ < Hg²⁺. This order is in agreement with their power of polarizability [45]. Being the biggest in the column, it is still believable that Hg²⁺ should fit into the ring very well. One prove is a crystal structure of complex between larger ion Pb²⁺ with *N,N'*-bis(2-aminobenzyl)-4,13-diaza-18-crown-6 (17) which clearly shows the penetration of Pb²⁺ into the crown ether ring (Figure 3.15) [43]. However, the trend is not kept when ligands are much bulkier. For example, the value of log β_{ML} for complexation of L4 with Cd²⁺ is one log unit higher than that with Hg²⁺ (4.68 vs. 3.62). Since d orbitals of these metal ions are filled, any energy changes resulting from different geometries should be minimized. The main factor that dominates the stability of Hg²⁺ complexes should be its ionic size. It should be more difficult for

bulky ligands to reorganize themselves for a larger ion, Hg^{2+} , than for a smaller ion, Cd^{2+} .

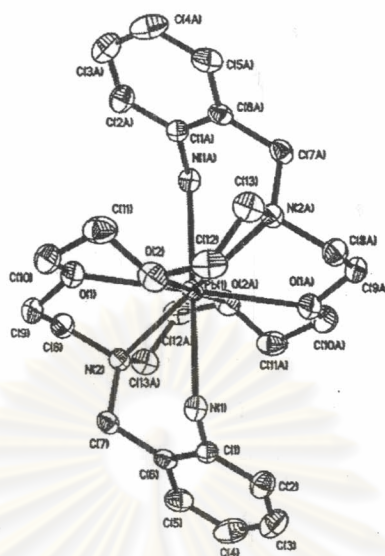


Figure 3.15 X-ray crystal structure of complex $[\text{Pb17}]^{2+}$ showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity. The ortep plot is at 30 % probability level [43].

As noted before, the largest-sized ion studied Pb^{2+} formed very stable ML complex with every ligand. The effect of metal ion size is seen from ML_2 formation nevertheless. The high stability of Pb^{2+} complexes might be explained by its size being more suitable to the cavity of diazacrown ethers than any other ion studied. It is very likely that Pb^{2+} ion, once fit into the cavity, would benefit the interactions from every donor atom in the cavity as recently proved by crystal structure in Figure 3.15. Besides ionic size, another factor is bonding type. Because this metal ion is classified as a representative element, the chemical bonds formed by Pb^{2+} should differ from those formed by other metal ions studied. This toxic metal should be bound to ligand by covalent bonds rather than by ion-dipole interactions. The consequence is that Pb^{2+} can form more stable complexes than can other metal ion studied, because the strength of covalent bonds is greater than is that of ion-dipole interactions.

3.4 Selectivity of ligands

It is important to be noted that the stability constants do not reflect the metal affinity of ligands. The direct comparison of these constants can be misleading. For a given complex equilibrium system, the concentration of unbound metal ion represents a direct gauge of the ligand-metal affinity with consideration of all involved equilibria. Thus, the comparison of the free metal ion concentration allows a direct comparison of various ligands [47]. The percentage of various free metal ions for each ligand obtained by calculation using program Haltafall [29] at $C_M = 1 \times 10^{-3} \text{ M}$, are given in Figure 3.16. Note that, for Pb^{2+} system, the lower limit of stability constant for UV-Vis spectrophotometry ($\log \beta_{ML} = 7$) was used in this calculation.

As can be seen below from Figures 3.16 and 3.17, many ligands prefer to bind Co^{2+} , especially **L2**, **L3**, and **L4**. On account of ML_2 formation, the higher extent of **L4** has to be used to completely bind Co^{2+} (% free metal = 0) compared to that of **L2** and **L3**: $C_L (\times 10^{-3} \text{ M}) = 2.4, 2, \text{ and } 1.6$, respectively. Due to low stability constants, the selectivity for Co^{2+} of **L1**, **L5**, and **L6** is slightly lower than is that of **L2**, **L3**, and **L4**. For other metal ions with the exception of Pb^{2+} , it is clearly seen from Figure 3.17 that not all ligands can bind them completely, notably Zn^{2+} . The calculation shows that it would take $5 \times 10^{-2} \text{ M}$ of **L2** to bind all of Zn^{2+} at $1 \times 10^{-3} \text{ M}$. Even a ligand that forms M_2L complex like **L4**, it still needs $3 \times 10^{-2} \text{ M}$ to completely take up Zn^{2+} at $1 \times 10^{-3} \text{ M}$, as shown in Figure 3.18. This could be of advantage though, because it means a selectivity of a particular metal ion over Zn^{2+} , e.g. the use of **L4** as host for selectively binding Cd^{2+} over Zn^{2+} . Usually Zn^{2+} , Cd^{2+} , and Pb^{2+} are found ubiquitously in the environment [41], and there is a report attempting to evaluate a selective binding of Cd^{2+} over Zn^{2+} [48].

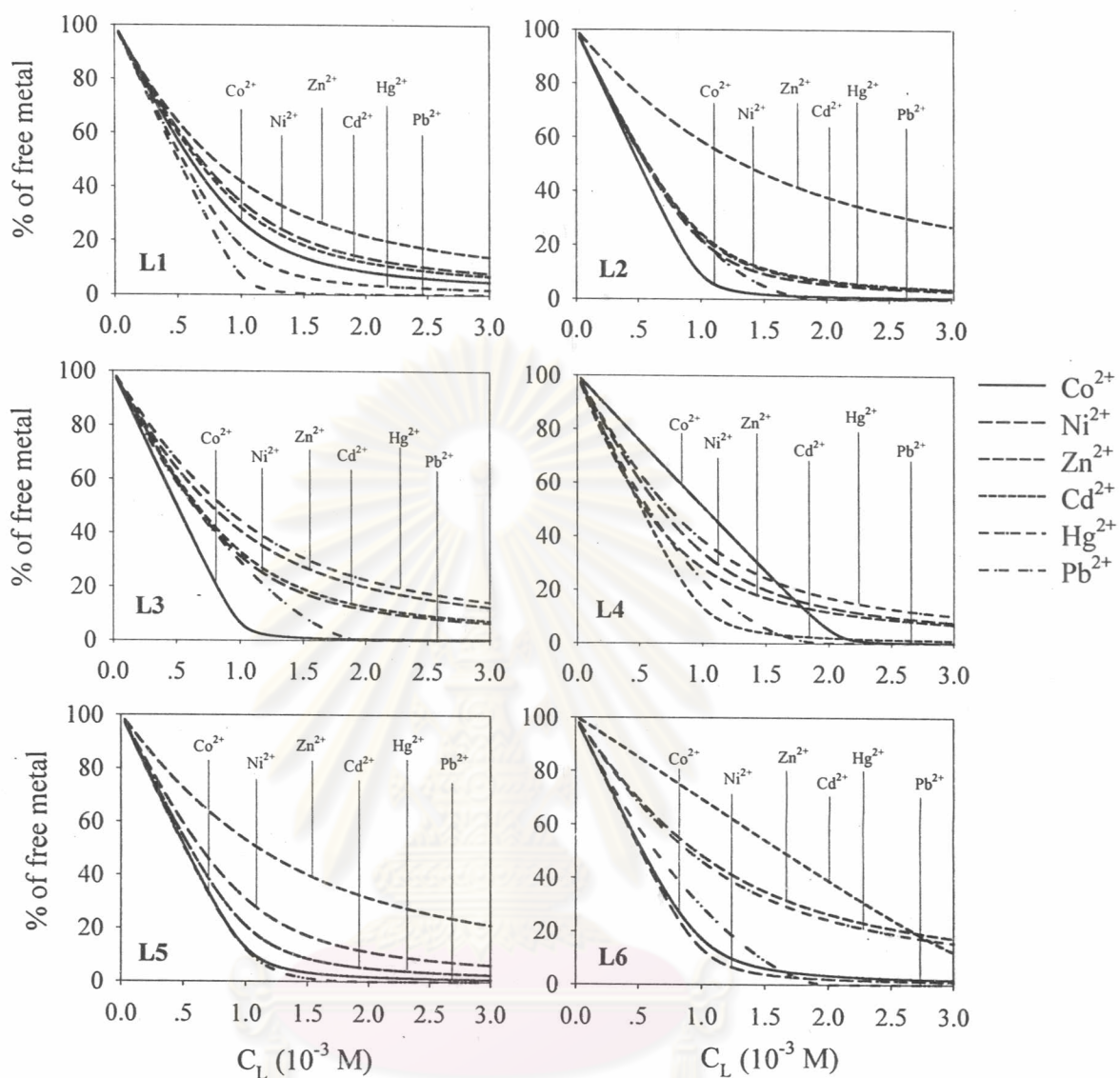


Figure 3.16 Percentage of free metal ions by each ligand studied as a function of ligand concentration ($C_M = 1 \times 10^{-3}$ M)

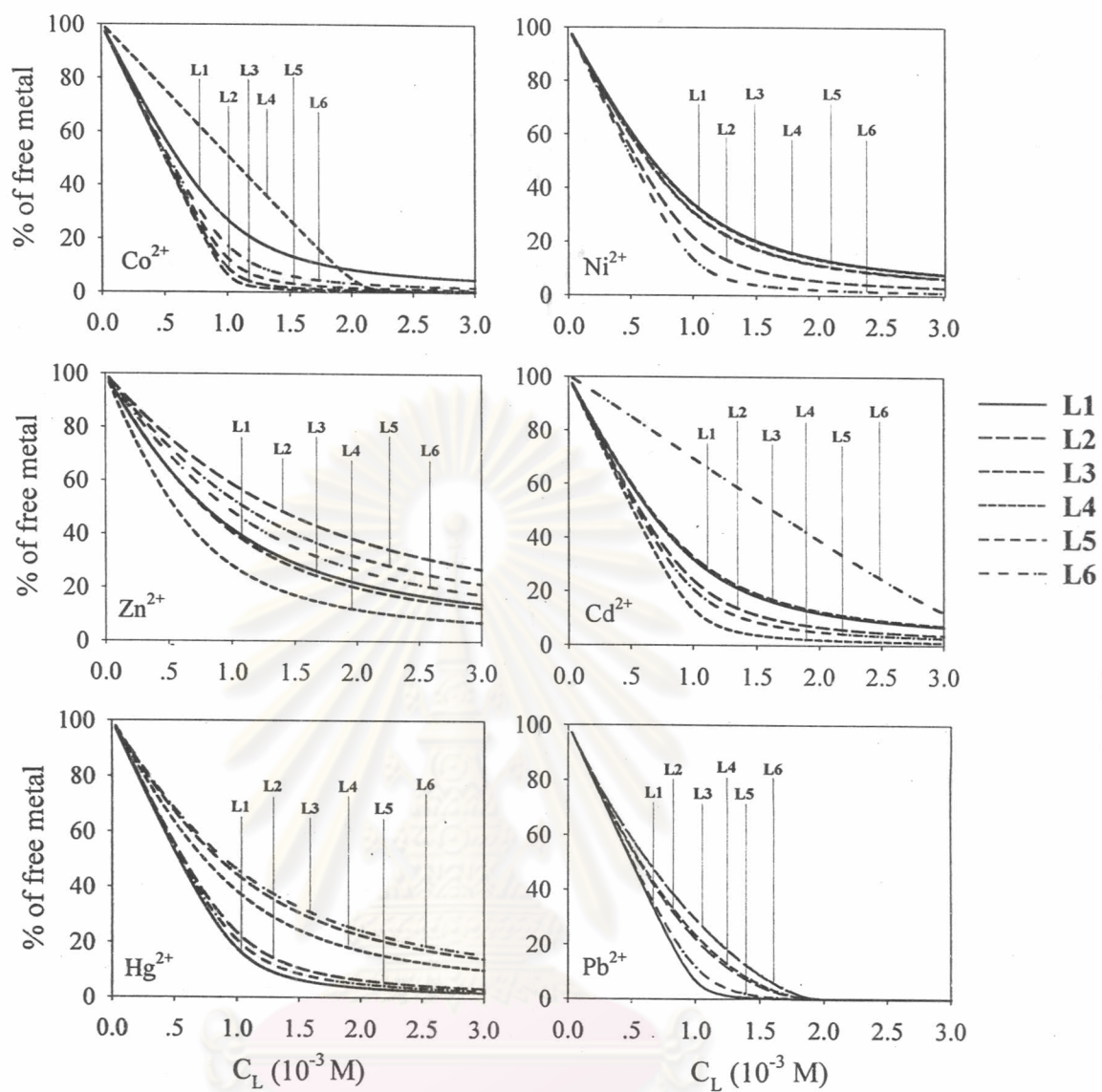


Figure 3.17 Percentage of free metal ions by each metal ion studied as a function of ligand concentration ($C_M = 1 \times 10^{-3}$ M)

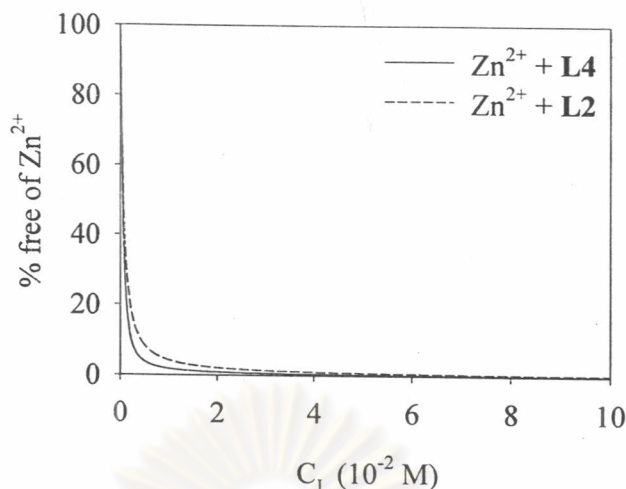


Figure 3.18 Percentage of free Zn^{2+} formed with either **L4** or **L2**

For Ni^{2+} , the great selectivity of **L6** for this ion is due to high stability constant among ligands studied. It is notable that the selective ability of ligand is in great agreement with the stability of complex. According to the evaluation by program Haltafall, the selectivity order corresponds well to the stability order ($\text{Zn}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+}$), even if M_2L formation in the case of Zn^{2+} is already taken into account. The exception for **L4** ($\text{Co}^{2+} < \text{Ni}^{2+} < \text{Zn}^{2+}$; at $C_L = 1.5 \times 10^{-3} \text{ M}$) is found in consequence of ML_2 formation with Co^{2+} as shown in Figure 3.16. Nevertheless, the normal trend is restored when $C_L > 1.5 \times 10^{-3} \text{ M}$. This proves that both complex stoichiometry and value of $\log \beta$ play an important role on the selectivity order.

In the case of heavy metals, stability constants of heavy metal complexes are fairly low compared to those of transition metal complexes, causing low selectivity. The exception is found in the case of Pb^{2+} , which form very strong complexes in all systems. All the ligands, of course, show high selectivity for this metal ion. They could completely bind Pb^{2+} at $C_L > 2 \times 10^{-3} \text{ M}$.

As demonstrated in Figure 3.16, some of ligands studied in this research bind Co^{2+} more preferably. Although the production of cobalt is usually subsidiary to that of nickel (about 20,000 tonnes in 1995) [17], it is toxic and has been widely used in industry. Cobalt is a technically important metal used mainly as a constituent of many alloys and as a binder in hard metal industry [49]. The instance of cobalt used as

catalyst is cobalt/manganese bromide catalyst. Every year 500 to 600 tonnes of cobalt are consumed to produce catalysts used in the production of more than 10 million tonnes of terephthalic acid and its derivatives per year [50]. In addition to the drawbacks of cobalt mentioned above, cobalt-alkyne complexes are used as drugs with remarkable cytotoxicity [51]. Due to its important role playing, attentions in the complex formation and the recovery of Co^{2+} have been considerably paid using ethylenediamine-*N,N,N',N'*-tetraacetanilide [52] and sodium-*N,N,N',N'*-tetrakis-(sodium carboxylate methyl)-2,6-diamino-cresolate [53] as hosts. Due to high selectivity for Co^{2+} and good properties of crown ether, some of the new macrocyclic ligands in this study may be applied as molecular hosts for Co^{2+} , especially, **L2** and **L3**. Note that there are few ligands applied as selective molecular receptor for Co^{2+} compared to other metals [54].

Due to detrimental effects of Pb^{2+} , its complexation is extensively studied using many ligands such as *N,N'*-bis(2-aminobenzyl)-4,13-diaza-18-crown-6 [43], *N,N'*-bis[(2-salicylaldimino)benzyl]-4,13-diaza-18-crown-6 [43], decamethylcucurbit[5]uril [55] and 7,16-dithenoyl-1,4,10,13-tetraoxa-7,16-diaza cyclooctadecane [56] as hosts, as well as 1,10-dibenzyl-1,10-diaza-18-crown-6 [42] as ion-selective membrane electrode. Since all ligands studied show high selectivity for Pb^{2+} , the novel ligands in this research may become new molecular hosts for Pb^{2+} .

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