

# CHAPTER I

## INTRODUCTION

### 1.1 Complex compounds

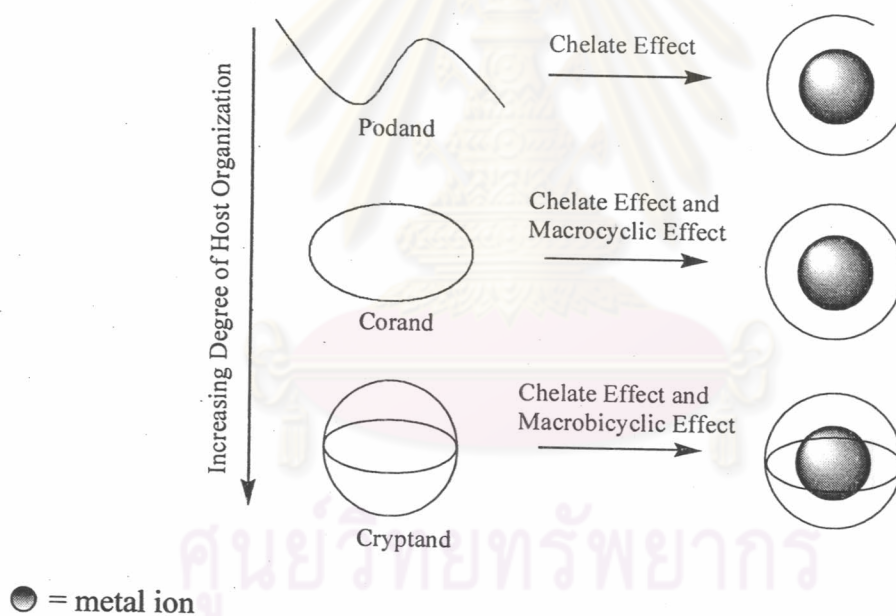
Complexes are compounds containing central atom(s), ion(s) or molecule(s), which is usually a metal ion but may be any electron acceptor (Lewis acid), and which is surrounded by several electron donor groups (Lewis bases) that are generally referred to as ligands. The complex, which may be either charged or neutral, tends to retain its identity even in solution, although both dissociation and replacement of the original ligands may occur. Complex compounds that contain one metal ion are called mononuclear complexes (ML) and that contain more than one metal ion are called polynuclear complexes ( $M_nL$ ).

#### 1.1.1 Chelate complexes

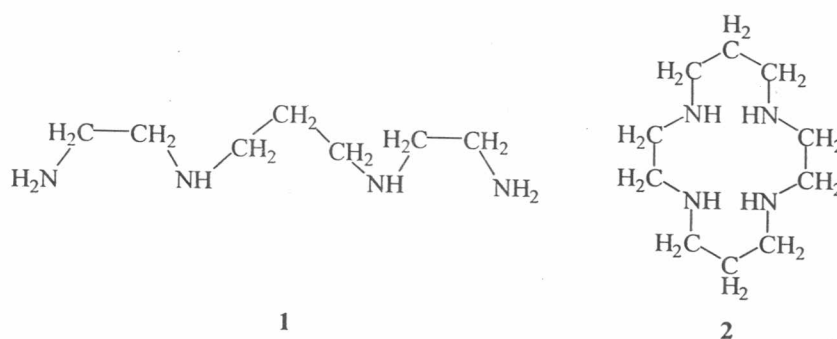
When a ligand, such as ethylenediaminetetraacetic acid (EDTA) or ethylenediamine, which can potentially coordinate to a metal ion through more than one position, acts as a multidentate ligand, the resulting complex is called a chelate complex. Chelate complexes are of particular importance because of their generally greater stability than the complexes of the corresponding unidentate ligands. This greater stability, known as the chelate effect, gives rise to their widespread applications in various chemical fields, for example, in complexometric titrations such as EDTA titrations [1] or in catalytic reaction such as the participation of crown ether derivatives for the migratory insertion of carbon monoxide in indenyl and cyclopentadienyl iron (II) complexes [2]. Chelating ligands can be classified into the following three categories, namely [3]:

- a. Podand: open-chained ligands, e.g. EDTA
- b. Corand: macrocyclic compounds, e.g. crown ether
- c. Cryptand: macrobicyclic compounds, e.g. cryptand

In supramolecular chemistry, ligands are called *hosts* while metal ions or other molecules that are bound by hosts are called *guests*. Host and guest molecules have together affected by H-bonds or by electrostatic interactions. Usually, topology of free hosts is arranged in order to diminish steric hindrance. When a certain guest appears in the system of one host, the former is incorporated to binding sites of the latter which will reorganize itself to give appropriate geometry for the guest. The order of degree of host organization is: Podand < Corand < Cryptand, which is shown in Figure 1.1. This is because Podand, Corand, and Cryptand can provide chelate, macrocyclic, and macrobicyclic effect for guests, respectively. The open chain polydentate ligand, tetramine **1**, and tetraaza 14-crown-4 commonly known as cyclam **2** are examples of Podand and Corand. Both molecular structures are depicted in Figure 1.2.



**Figure 1.1** The chelate, macrocyclic and macrobicyclic effects



**Figure 1.2** Molecular structures of tetramine (1) and cyclam (2)

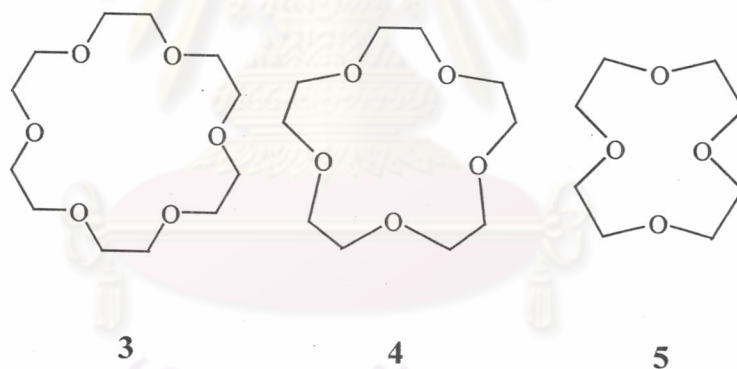
Both molecular structures above contain similar donor atoms but their degrees of ligand organization are different. Complexations of ligand **1** need to employ higher energy for its reorganization while those of ligand **2** can easily reorganize itself to bind a certain guest. Thus ligand **2** forms more stable complexes with given metal ions than the corresponding open-chained ligand **1**.

The most important factor that gives rise to the macrocyclic effect is the influence of complex formation on the solvation terms. Although the metal complexes of the macrocyclic and open-chained ligands are similarly solvated, the free macrocyclic ligand is unable to accommodate as many hydrogen-bonded water molecules as its open-chained counterpart, and thus less desolvation of the macrocyclic ligand occurs on complex formation. Since the macrocyclic effect arises largely from ligand solvation effect, it is largely independent on metal ion so long as the macrocyclic ligand does not attempt to impose a geometry different from that of the open-chained ligand. In addition, the magnitude of macrocyclic effect decreases in solvents which only weakly solvate dissolved species. An understanding of the origins of the macrocyclic effect should be of value in unravelling the complexities of the interaction of metal ions with large biological molecules, such as proteins and enzymes, where solvation terms play a very important role in determining the nature and extent of complex formation.

## 1.2 Crown ethers

Cyclic polyethers, commonly named *crown ether* and first discovered in 1967 by Charles Pedersen [4], are composed of ether functional groups that can function as electron donors. Therefore, they have been effectively used as chelating ligands to form ion-dipole interactions with metal ions. In the past forty years, the study involving crown ethers and other macrocyclic ligands has expanded from a chemical curiosity to a major area of research [5] and has been considerably published [6-10]. The use of monoaza-18-crown-6 derivative as host for cations, e.g.  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Pb}^{2+}$  is an example of numerous applications of crown ether [11].

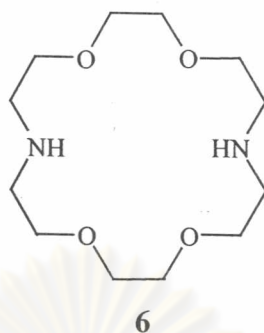
Nomenclature of crown ether is usually in the form of x-crown-y where x is the number of total atom in the crown unit and y the number of oxygen atoms or heteroatoms. Crown ethers containing only oxygen donor atoms are generally called oxacrown ether. Some examples of these compounds are shown in Figure 1.3.



**Figure 1.3** Examples of crown ethers: 18-crown-6 (3), 15-crown-5 (4), 12-crown-4 (5)

The differences in the cavity size and number of oxygen donor atoms among ligands 3, 4, and 5 can influence the binding affinity. For example, compound 3 prefers  $\text{K}^+$  to other alkali ions but compound 4 prefers  $\text{Na}^+$ . This relationship can be explained by size match between the crown cavity and a metal ion. The cavity of 18-membered ring 3 is the most comparable in size to ionic radius of  $\text{K}^+$  among alkali ions; that of 15-membered ring 4 is likewise to ionic radius of  $\text{Na}^+$ .

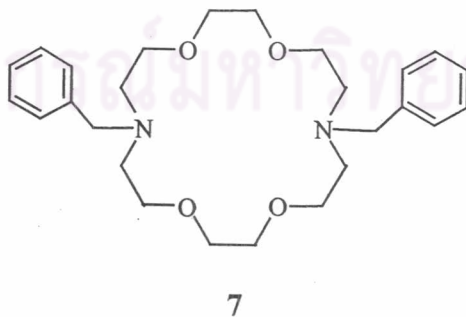
Another important crown ether derivative, shown in Figure 1.4, which contains nitrogen donor atoms in the macrocyclic ring is recognized as azacrown ethers.



**Figure 1.4** Molecular structure of diaza-18-crown-6

Azacrown ether derivatives having soft binding sites can improve binding abilities for soft metal ions. For instance, ligand **6** forms more stable complex with  $Pb^{2+}$  than with  $K^+$  [3]. The complexation of diaza crown ether having melamine side arms with alkali and transition metal ions studied by Quici and co-workers [12] showed that the higher affinities for transition metal cations of azacrown ethers compared to oxacrown ether was due to covalent contributions where N(s) of crown ether affect vacant d orbital of transition metal ions.

Hamamci and co-workers [13] studied complexation of ligand as shown in Figure 1.5 with alkali ions. This crown ether may be called *bibracchial lariat ether* (BiBLE) which refers to crown ethers or similar macrocyclic derivatives with one or more accompanying side arms.



**Figure 1.5** Molecular structure of 4,13-*N,N'*-dibenzyl-diaza-18-crown-6

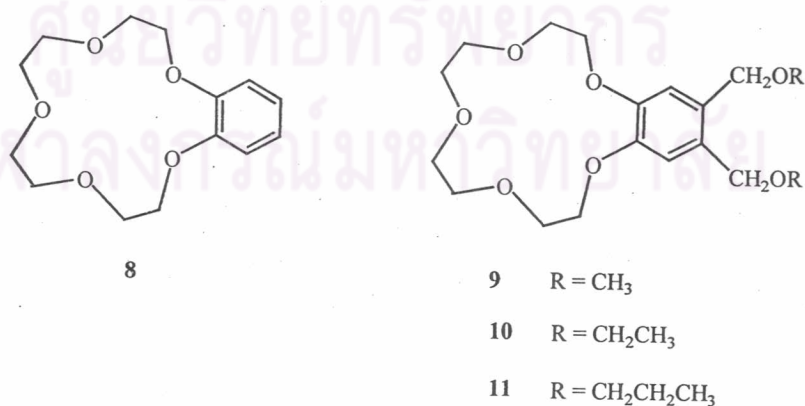
Hamamci and co-workers found that crown ether **7** could be employed in selective solvent extraction of  $\text{Li}^+$  from other alkali ions [13]. This is contrast to a general occurrence, where 18-membered crown ether prefers  $\text{K}^+$  to other alkali ions. This study indicated that side arms had improved binding affinity for  $\text{Li}^+$ , due to steric hindrance of side arms.

In principle, side arm arrangements of bibracchial crown ether are *anti* and *syn* arrangement as shown in Figure 1.6 [14].

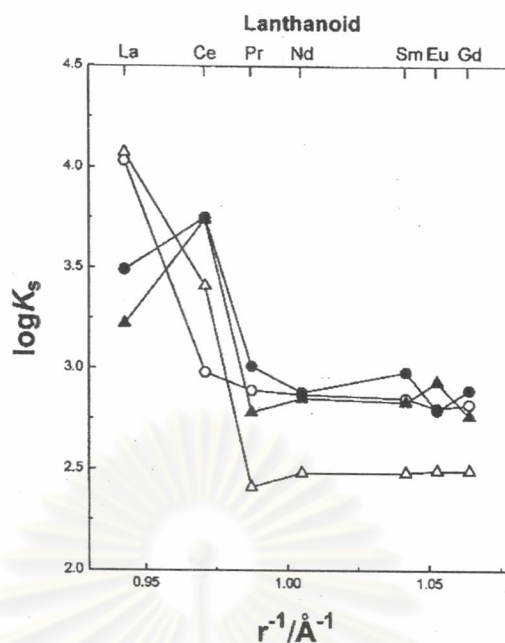


**Figure 1.6** Anti and syn arrangements in bibracchial lariat ethers.

Liu and co-workers [15] studied complexation of double-armed benzo-15-crown-5 lariats shown in Figure 1.7 with light lanthanoid nitrates ( $\text{M}(\text{NO}_3)_3$ ;  $\text{M} = \text{La}$ ,  $\text{Ce}$ ,  $\text{Pr}$ ,  $\text{Nd}$ ,  $\text{Sm}$ ,  $\text{Eu}$ , and  $\text{Gd}$ ) in acetonitrile. They reported that an introduction of ether side arms to **8**, affording double-armed lariat **9**, **10**, and **11**, could alter the original binding ability for cations as shown in Figure 1.8.



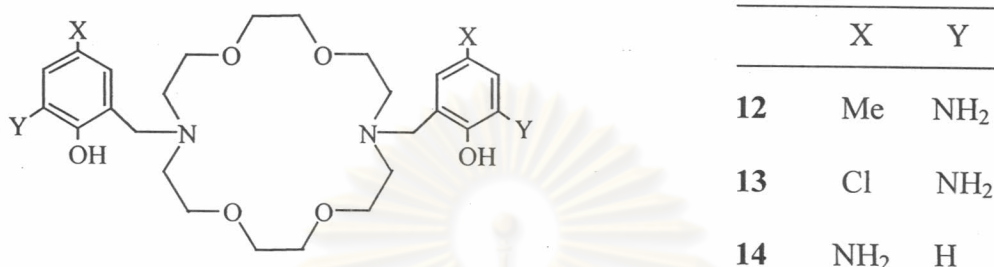
**Figure 1.7** Molecular structure of benzo-15-crown-5 lariat ether and its derivatives



**Figure 1.8** Complex stability constant ( $K_s$ ) as a function of reciprocal ionic radius ( $r^{-1}$ ,  $\text{\AA}^{-1}$ ) for the complexation of light lanthanoids with **8** ( $\Delta$ ), **9** ( $\circ$ ), **10** ( $\bullet$ ), and **11** ( $\blacktriangle$ ) in acetonitrile at 25 °C

While stability constants ( $K_s$ ) of complexation between  $\text{La}^{3+}$  with ligands **8** and **9** were fairly equal, stability constant of  $\text{Ce}^{3+}$  with **8** was higher than that with **9**. In contrast, other ions in this series formed more stable complexes with **9** than with **8**. The highest cation selectivity for  $\text{La}^{3+}$  by **9** could be attributed to the appropriate steric requirement upon side arm ligation. In the cases of **10** and **11**, significant changes in binding behavior of particular  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  complexes were found. According to binding abilities of ligands **9-11**, the relative cation selectivity between  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  was dramatically inverted just by extending the side arms, switching from the  $\text{La}^{3+}/\text{Ce}^{3+}$  selectivity of **11** for **9** to the  $\text{Ce}^{3+}/\text{La}^{3+}$  selectivity of 3.3 for **11**. It can be deduced from experimental results that the overall steric hindrance around the benzene ring and the side arm donors play an important role in determining the spacial arrangement and orientation of the donor atoms.

Bradshaw and co-workers [6] studied complexation of phenolic diaza-18-crown-6, molecular structure shown in Figure 1.9, with alkali and transition metal ions. Their experimental results showed that these ligands had formed more stable complexes with  $\text{Cu}^{2+}$  than with  $\text{Na}^+$  and  $\text{K}^+$ , which could be explained by hard and soft acid-base theory.

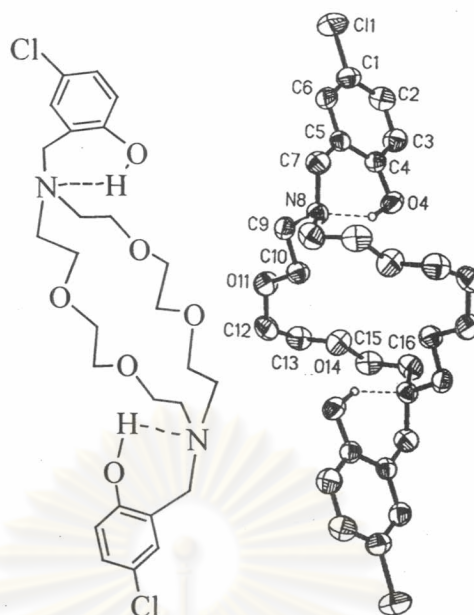


**Figure 1.9** Molecular structure of phenolic diazacrown ether derivative

Using hard and soft acid-base theory, it can be concluded that oxacrown ethers prefer binding with alkali or alkali earth ions to binding with transition metal ions. Alternately, diazacrown ethers preferably bind to transition metal ions than to alkali and alkali earth ions [3].

Izatt and co-workers [16] studied complexation of 4-chlorophenol-substituted azacrown ethers **15** with alkali, alkali earth, and transition metal ions using calorimetric titration. Molecular structure of free ligand is shown in Figure 1.10. Experimental results indicated that ligand **15**, whose core molecular structure is similar to crown ether studied in this thesis, has higher affinity for transition metal ions than for other metal ions, except  $\text{Ca}^{2+}$ .





15

**Figure 1.10** Molecular structure and computer drawing of **15**

It is found from X-ray crystallographic data that there are H-bonds between hydrogen groups and nitrogen atoms as shown in Figure 1.10. Deactivation of crown nitrogens by hydrogen bonding with the OH groups would weaken interaction with the alkali metal cations. Because of the structure similarity of ligand **15** and ligands studied in this research (*vide infra*), it might be deduced that intramolecular H-bonds should take place likewise in the systems studied in this research.

It can be concluded from numerous literatures that substitution of oxygen atoms to nitrogen atoms and an introduction of pendant groups into macrocyclic ring can improve both affinity and selectivity of the ligand.

### 1.3 Choosing techniques for determination of stability constants [1]

A large number of stability constants have been determined, but a considerable proportion of these is of doubtful accuracy. Therefore it is important that great care is taken before measuring stability constant to ensure that the experimental method will give a reliable result.

Experimental methods for determining stability constants fall into two broad groups:

- a. Methods in which the observable is proportional to the number of molecules of a given type present; all spectroscopic methods fall into this groups.
- b. Methods in which the observable is proportional to the activity of the molecules of a given type; most electrochemical and distribution methods fall into this group.

Spectrophotometry provides an additional method for comparing several possible chemical models not available with potentiometry. Choice of suitable wavelengths enables each species to make a direct contribution to the measured data. However, because the UV-Vis spectra of most complexes contain broad overlapping absorption bands, parameter correlation consequently arises and it is not usually possible to evaluate stability constants as precisely from spectrophotometric as from potentiometric data. Unfortunately, there are occasions where potentiometry is unable to discriminate between equilibria. Moreover, method requires a suitable electrode system, so many reactions cannot be studied potentiometrically.

The ideal approach is to combine spectrophotometric and potentiometric data, using the former for defining the chemical model and both for evaluation of the stability constants.

#### 1.4 The importance of metal ions studied

Metallic elements can be classified into three principal categories, i.e. main group, transition, and heavy metals. This study focuses on some of two latter categories, i.e.  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Pb}^{2+}$ . Because some of these elements are toxic, so methods concerning extracting, separating, and recovering them need to be developed. All of the seven metal ions studied in this thesis are completely important to either biology or environment. The group of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  are very important in biochemistry and are essential metal ions for human beings. The group of  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Pb}^{2+}$  are recognized as toxic metal ions that are very dangerous for human beings, for example the Minamata disaster in Japan, where 52 people died in 1952, were caused by abnormally high concentrations of mercury in

the form of MeHgSMe in fish [17]. Thus many studies of complexation of these metal ions with various ligands have been reported [18-21]. This research is to study their complexation with new crown ether derivatives.

### 1.5 Objective of this research

The objective of this work is to determine the stability constants of six diazacrown ether derivatives and seven transition and heavy metal ions in MeOH by UV absorption spectrometric titration. Stability constants could be obtained from monitoring variations of UV absorption and were refined using program Sirko [22]. Stoichiometry of each complex studied and their stability constants will be reported and discussed. The ligands that possess high affinity for certain metal ions and/or unique complexing absorption may be developed as metal ion chemosensors.



ศูนย์วิจัยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย