การตรวจสอบความเป็นเบสของสารประกอบคาลิกซ์[4]-ไซเคลน-เบนโซ-คราวน์-6 และ
เสถียรภาพของสารประกอบเชิงซ้อนกับโลหะไอออนโดยวิธีโพเทนชิออเมทริก

นางธนาพร บุญชู

INVESTIGATION OF BASICITY OF CALIX[4]-CYCLEN-BENZO-CROWN-6 AND STABILITY OF ITS COMPLEXES WITH METAL IONS BY POTENTIOMETRIC METHOD

Mrs. Thanaporn Boonchoo

A Thesis Submitted in Partial Fulfillment of the Requirements

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Thesis Title   Investigation of Basicity of Calix[4]-cyclen-benzo-crown-6 and Stability of Its Complexes with Metal Ions by Potentiometric Method

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ธนาพร บูญชู : การตรวจสอบความเป็นเบสของสารประกอบคาลิกซ์[4]-ไซเคลน-เบนโซ-คราวน์-6 และเสถียรภาพของสารประกอบเชิงซ้อนกับโลหะไอออนโดยวิธีโพเทนชิออเมทริก (INVESTIGATION OF BASICITY OF CALIX[4]-CYCLEN-BENZO-CROWN-6 AND STABILITY OF ITS COMPLEXES WITH METAL IONS BY POTENTIOMETRIC METHOD) อ. ที่ปรึกษา : รศ.ดร.วิทยา เรืองพรวิสุทธิ์, อ. ที่ปรึกษาร่วม : ผศ.ดร.บัญชา พูลโภคา, 64 หน้า. ISBN 974-17-2141-2.

การหาค่าคงที่โปรโตเนชันของสารประกอบคาลิกซ์[4]-ไซเคลน-เบนโซ-คราวน์-6 ใน 1 x 10^{-2} M $Bu_4NCF_3SO_3$ ใน 40% CH_2Cl_2/CH_3OH ที่ 25 °C โดยวิธีโพเทนชิออเมทริกไทเทรชัน พบว่า log K_1 = 10.91±0.13, log K_2 = 10.30±0.25, log K_3 = 6.24±0.26 และ log K_4 = 2.55±0.28 การหาค่าคงที่ความเสถียรของสารประกอบเชิงซ้อนระหว่างสารประกอบคาลิกซ์[4]-ไซเคลน-เบนโซ-คราวน์-6 กับไอออน Cu(II) และ Zn(II) โดยวิธียูวีวิสสเปกโตรโฟโตเมทริกไทเทรชัน พบว่าค่าคงที่ความเสถียรของสารประกอบเชิงซ้อน CuL^{2+} และ ZnL^{2+} มีค่า log β เท่ากับ 4.37 และ 3.45 ตามลำดับ ค่าพลังงานเสถียรของการเกิดสารประกอบคาลิกซ์[4]-ไซเคลน-เบนโซ-คราวน์-6 กับ โปรตอน และ โลหะไอออน Zn(II) โดยวิธี แอบอินิชิโอ ฮาทรี-ฟอกค์ ด้วยเบซิสเซ็ต 6-31G พบว่า ΔE_1 = –290.1 kcal/mol, ΔE_2 = -205.0 kcal/mol, ΔE_3 = -124.9 kcal/mol และ ΔE_4 = –26.9 kcal/mol พลังงานของการเกิดสารประกอบเชิงซ้อนกับโลหะไอออน Zn(II) มีค่าเท่ากับ -370.3 kcal/mol

ภาควิชา …………เคมี………… ลายมือชื่อนิสิต ....
สาขาวิชา…………เคมี………… ลายมือชื่ออาจารย์ที่ปรึกษา ....
ปีการศึกษา …… 2545………… ลายมือชื่ออาจารย์ที่ปรึกษาร่วม ....

Protonation constants of calix[4]-cyclen-benzo-crown-6, L in 1×10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH at 25 °C determined by potentiometric titration are $\log K_1 = 10.91 \pm 0.13$, $\log K_2 = 10.30 \pm 0.25$, $\log K_3 = 6.24 \pm 0.26$ and $\log K_4 = 2.55 \pm 0.28$. Stability constants for the ligand L complexes with Cu(II) and Zn(II) in 1×10^{-2}M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH at 25 °C were determined by UV-VIS spectrophotometric titration. The stability constants of the Cu(II)/L and Zn(II)/L complexes as $\log \beta$ are 4.37 and 3.45, respectively. Stabilization energies for protonations of the ligand L form the calculation by *ab initio* Harthree-Fock with 6-31G basis set are $\Delta E_1 = -290.1$ kcal/mol, $\Delta E_2 = -205.0$ kcal/mol, $\Delta E_3 = -124.9$ kcal/mol and $\Delta E_4 = -26.9$ kcal/mol and complexation energies of Zn(II) complexes with ligand L are -370.3 kcal/mol.

Department ……..…chemistry………   Student's signature ……………………….

Field of study……....chemistry………   Advisor's signature ……………………….

Academic year……….2002………….   Co-advisor's signature …………………...

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LIST OF ABBREVIATIONS

°C	Degree Celcius
M	Molar
β	Overall stability constant
K	Stepwise stability constant
mM	Milimolar
C_L	Concentration of ligand
A_L	Absorbance of ligand

CHAPTER I

INTRODUCTION

1.1 Macrocyclic ligands and cyclic supermolecules

Macrocyclic ligands consist of donating atoms connecting with alkyl or aryl chains in a cyclic manner. The macrocyclic compounds containing electron donating atoms such as nitrogen, oxygen, and sulfur, called as aza, oxa, and thia compounds respectively, have ability to bind cations. The metal ion and host-guest chemistry of macrocyclic ligands have been developed rapidly over recent years and now impinges on wide areas of both chemistry and biochemistry. The complexation is principally controlled by the structural features of the ligand cavity and size of the cation. The oxidation number and the size of cation usually indicate the stability of complexes.[1]

Affinities of complexing properties of macrocyclic ligands depend on some important properties of the ligand such as:

1. The relative cation and ligand cavity sizes

2. The bonding sites within the macrocyclic compound such as nitrogen (-aza compounds), oxygen (-oxa compounds) and sulfur (-thio compounds)

3. The oxidation number and the size of cation or other guests

4. Steric hindrance

5. Solvent effect.

In 1960s, Perderson[2] has found crown ethers, which are the two-dimension macrocyclic ligands. Until now, the macrocyclic ligand is a continuous interest in the synthesis and the complexation properties of the crown compounds. In 1983, Gutsch *et al*.[3] Report the synthesis of calix[4]arene by condensation reactions.

1.1.1 Crown ethers

Crown ethers are two-dimensional macrocyclic molecules that can form complexes with metal ions and organic cations by oxygen atoms. The affinity of complexes depends on the fitting of cavity of crown ether and metal ion. Crown ethers can be designed to be a cation receptors and transporting agents, which can bind selectively toward particular cations.[4-7]

18-crown-6   dibenzo-18-crown-6
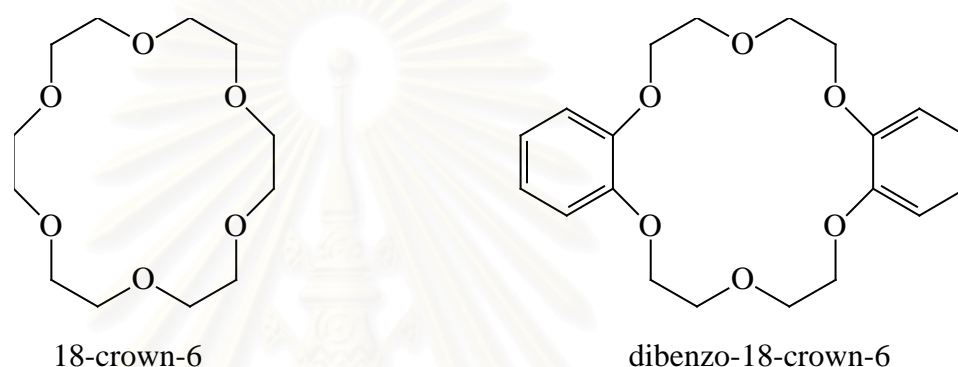
Figure 1.1 Some examples of crown ethers.

1.1.2 Macrocyclic polyaza compounds

The coordination chemistry of amines has undergone a considerable development since the first use of amines as a ligand. Tetraazacycloalkanes, especially cyclen (Figure 1.2) and cyclam derivatives, have been most extensively studied because of these tetraazamacrocycles are able to form highly stable complexes with transition metal cations, lanthanide and actinide cations including organic or inorganic anions, with the exact behavior depending on the cavity size and the nature of substituents. The presence of four secondary amine functions on molecules allows for unlimited derivatization of these compounds. This versatility makes possible for the use of azacrown such as purification of waste water, catalysis and medicinal purposes.[8-9]
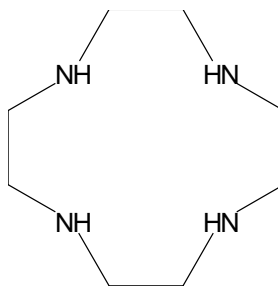
Figure 1.2 The macrocyclic tetraaza compounds, cyclen.

1.2   Calixarenes

Calixarenes have proved to be very useful building blocks in supermolecular chemistry. They are the cavity-containing-cyclic molecules made up of phenolic units linked *via* methylene bridges. The name *calixarenes* is chosen for this compounds because it clearly describes the shape of these cyclic molecules (calix: beaker, arene: aryl[10]) when they orientate in the cone conformation. Such conformation is very stable because of intramolecular hydrogen bondings of all phenolic hydroxy groups. Calixarenes possess an upper rim defined by the para substituents of the phenolic moieties and a lower rim defined by the phenolic hydroxy groups. One of the most important properties of calixarenes is their ability to include smaller molecules and ions reversibly and selectively. Calixarenes have many size of cavity for including substrates depending on the number of phenolic moieties. Calix[4]arene, the smallest number of this family, is a very popular one since it provides a cavity and can be prepared with ease. In addition they have different positions that can be selectively functionalized *i.e.*, the phenolic oxygens at the lower rim and the aromatic *para* positions at the upper rim. Calix[4]arene can adopt four different conformations: cone, partial cone, 1,2-alternate and 1,3-alternate[10], shown in Figure 1.3. This enlarges the number of potentially useful geometries of these molecules as building blocks. Calixarenes and especially calix[4] arenes are widely used in supramolecular chemistry because they are useful in the design and synthesis of artificial receptors for the selective recognition of ions and neutral molecules. Some of the molecular complexes of calixarenes are a class of inclusion compounds in which the receptors enclose other molecules without the formation of covalent or ionic bonds. Molecules whi   do the enclosing are referred

as hosts, while inducing molecules are guests. The hosts form a lattice type structure with voids, which are large enough to accommodate the guests.

Cone

patial cone

1,2-alternate

1,3-alternate
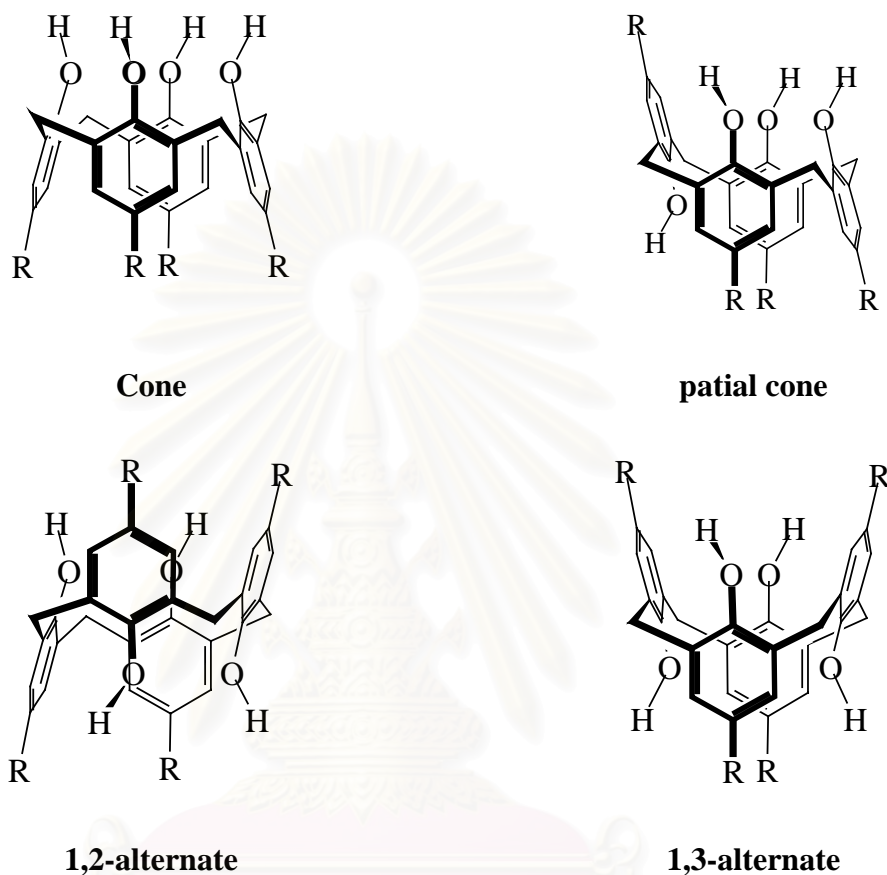
Figure 1.3   The conformations of calix[4]arenes.

In 1993, Ruangpornvisuti et al.[11] have determind the stability constants of complex of diaza-benzo-crown-*p-tert*-butylcalix[4]arene by potentiometric titrations and ultraviolet spectroscopic titrations. In 1999, Navakun [12] have determind the stability constants of 25,27-({2,2'-diethyl}benzyl)-3,7-dithianone-p-tert-butylcalix[4] arene complexs by potentiometric titrations.

1.3   Quantum Calculations for Calixarenes

In 1988, Ruangpornvisuti et al.[13] have determind the stability constants of lithum and magnesium complexes of cyclen by potentiometric titration, *ab initio* calculations on the protonated species of cyclen and its magnesium complexes. In 1995, Grootenhuis et al.[14] have studied some properties of calix[4]arene such as structural, energetical and acid-base properties by various computational methods. Due to conformational interconversion of calix[4]arenes, quantum calculations using CHARMM force field were employed to study the energy of each conformation and pathway of interconversion processes.
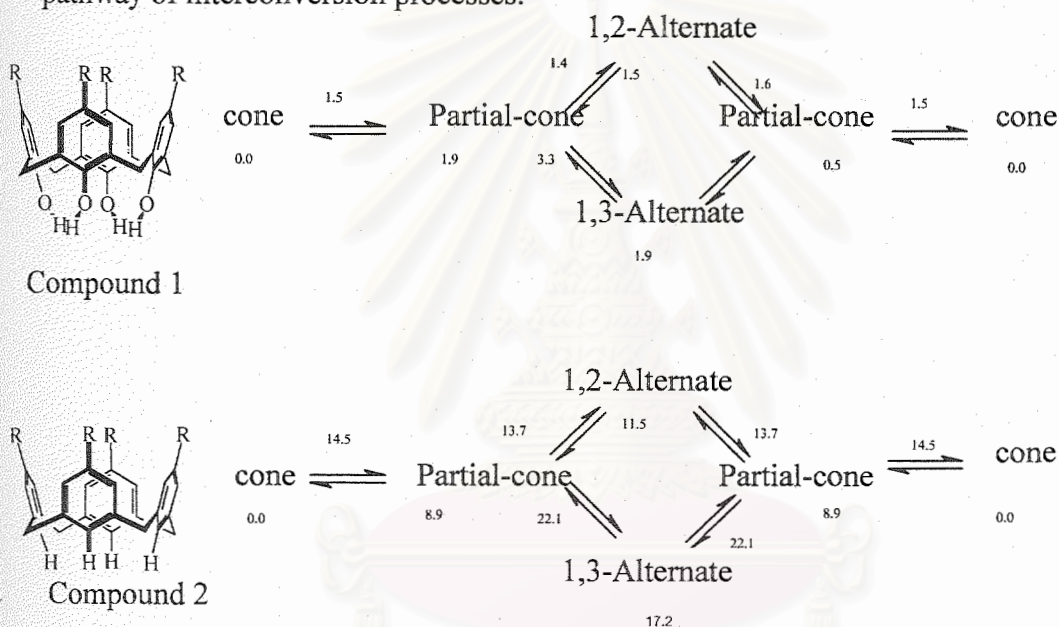
Figure 1.4   Interconversion between various conformations of calix[4]arenes. Energies in kcal mol^{-1}.

In 1999, Suwattanamala et al.[15] reported the protonation energies of copper and mercury complexes of 25,27-{2,2'-[(2,5,8-triaza)nonyl)diphenoxy]diethyl}-*p-tert*-butylcalix[4]arene have been calculated by semi-empirical (PM3) and *ab initio* method. In 1999, Cabral et al,[16] have calculated the stability conformers of calix[4]arene by *ab initio* method and the most stable conformer of cone was reported.

1.4   Objective and Scope of The Research

Calix[4]-cyclen-benzocrown-6, **L** is a newly synthesized compound and contains four nitrogen donor atoms for binding transition metal ion and a crown-6 unit for binding alkali cations. (Figure 1.5). Studies of basicity of calix[4]-cyclen-benzocrown-6, **L** and its complexation with some metal ions have been investigated by potentiometric and UV-VIS spectrophotometric titrations, respectively. The results of this research should lead to protonation ability of the calix[4]-cyclen-benzocrown-6, **L** and complexing ability of its complexes with some metal ions. Nowadays, the quantum chemical calculations play a singnificant role in chemistry. Therefore, energy of **L** and its protonation have been investigated using quantum chemical calculations provided in Guassian94W software.[17]   In addition, the knowledge of this research may lead to application of this ligand for metal ions separation from environment in the future.
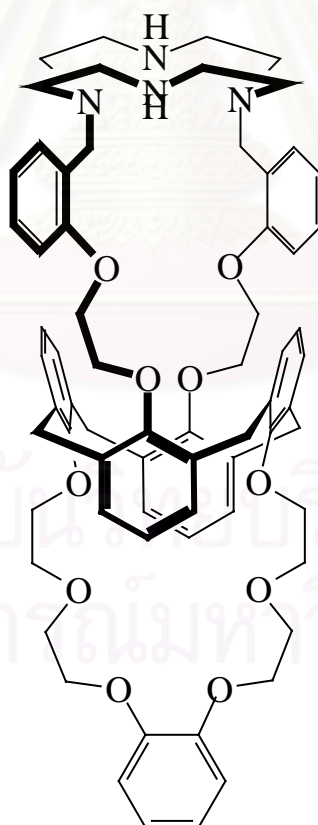
Figure 1.5   Calix[4]-cyclen-benzocrown-6.

CHAPTER II

THEORY

2.1   Equilibrium Potentiometry

2.1.1 Concentration Constants and Activity Constants

An equilibrium constant is quotient involving the concentrations or activities of reacting species in solution at equilibrium. Generally it is defined as ratio of the product of the activities *a* of the reaction products, raised to appropriate power, to the products of the activities of reactants, raised to appropriate power, illustrated by equation (2.1) where a, b, c and d are the stoichiometric coefficients of the solution species A, B, C and D respectively.

$$aA \;+\; bB \;\rightleftharpoons\; cC \;+\; dD \qquad Keq \;=\; \frac{a_C^{\,c}\; a_D^{\,d}}{a_A^{\,a}\; a_B^{\,b}} \qquad (2.1)$$
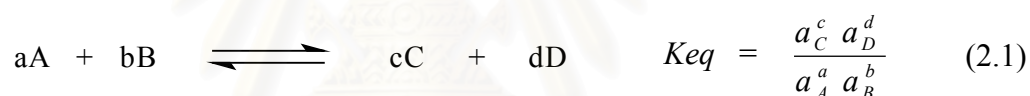
The determination of activities of complex ionic species at both infinite solution and in real solution is a complicated and time-consuming task. Hower concentrations are related to activities by the expression

$$a_x \;=\; [X]\gamma_x \qquad\qquad (2.2)$$

where a_x, $[X]$, and γ_x are activity, concentration and activity coefficient of X respectively. Activity coefficients of reacting species are in general tedious and difficult to measure. They also depend very significantly on the nature and concentrations of other species present in solution so that it is not possible to build universal tables of activity coefficients. Theoretical attempts at calculating activity coeffients, based on the Debye-Huckel approach and its extentions, are at best of only limited accuracy. Substituting the activities from equation (2.2) in (2.1), then the equilibrium constant can be rewritten as follow.

$$K_{eq} \quad = \quad \frac{a_C^c \, a_D^d}{a_A^a \, a_B^b} \quad = \quad \frac{[C]^c \, [D]^d}{[A]^a \, [B]^b} \cdot \frac{\gamma_C^c \, \gamma_D^d}{\gamma_A^a \, \gamma_B^b} \tag{2.3}$$

where [] indicates molar concentrations. If now it is possible to ensure that the

term $\quad \dfrac{\gamma_C^c \, \gamma_D^d}{\gamma_A^a \, \gamma_B^b} \quad$ remains constant then the term $\quad \dfrac{\gamma_C^c \, \gamma_D^d}{\gamma_A^a \, \gamma_B^b} \cdot K_{eq} \quad$ is also a constant.

Therefore, the equilibrium constant expressed in terms of the reacting species, called equilibrium concentration constant, K_c can be written as indicated by equation (2.4).

$$aA \; + \; bB \; \rightleftharpoons \; cC \; + \; dD \qquad K_c \; = \; \frac{[C]^c \, [D]^d}{[A]^a \, [B]^b} \tag{2.4}$$

Equilibrium concentration constant, K_c is also known as the stoichiometric equilibrium constant which determined at constant ionic strength where as K_{eq} is indicated by equation (2.1) which is known as an equilibrium activity constant or thermodynamic equilibrium constant.

The term $\quad \dfrac{\gamma_C^c \, \gamma_D^d}{\gamma_A^a \, \gamma_B^b} \quad$ in equation (2.3) may be effectively constant by, having

a large excess of an inert background electrolyte present and using only low concentrations of reacting ionic species so that any change in their concentrations as a result of their reaction together has an inisgnificant change on the overall ionic strength of the medium. It is generally possible to replace about 5% of the ions in the inert background electrolyte without appreciably altering the activity coefficiens of the minor species present. However, in recording a stoichiometric equilibrium constant it is essential to record not only the concentration of the inert background electrolyte, but also its nature, since the activity coefficient depend on the electrolyte. Consequently, of course, in comparing stoichiometric equilibrium constants, only data obtained under very conditions should be used unless the differences between the equilibrium constants are large.

2.2   Analysis Data

2.2.1 Protonation Constants

The acid-base equilibria of the ligands can be treated by protonation and disprotonation constant. Protonation constant is the equilibrium constant for the addition the nth proton to a charged or uncharged ligand. Protonation constant is know as basicity constant. The reciprocal of protonation constant is called disprotonation constant and defined as the equilibrium constant for the splitting off n^{th} proton from a charged or uncharged ligand. Disprotonation constant is also know as acidity constant. The following equations define these constants and show their interrelation.

$$L \; + \; H \; \rightleftharpoons \; LH \quad : \quad K_1 \; = \; \frac{[LH]}{[L][H]} \tag{2.5}$$

$$LH \; + \; H \; \rightleftharpoons \; LH_2 \quad : \quad K_2 \; = \; \frac{[LH_2]}{[LH][H]} \tag{2.6}$$

$$LH_2 \; + \; H \; \rightleftharpoons \; LH_3 \quad : \quad K_3 \; = \; \frac{[LH_3]}{[LH_2][H]} \tag{2.7}$$

$$\vdots \qquad\qquad\qquad \vdots$$

$$LH_{n-1} \; + \; H \; \rightleftharpoons \; LH_n \quad : \quad K_n \; = \; \frac{[LH_n]}{[LH_{n-1}][H]} \tag{2.8}$$

Another way of expressing the equilibria relations can be shown as follow:

$$L \; + \; H \; \rightleftharpoons \; LH \quad : \quad \beta_1 \; = \; \frac{[LH]}{[L][H]} \tag{2.9}$$

$$L \; + \; 2H \; \rightleftharpoons \; LH_2 \quad : \quad \beta_2 \; = \; \frac{[LH_3]}{[L][H]^2} \tag{2.10}$$

$$L \; + \; 3H \; \rightleftharpoons \; LH_3 \quad : \quad \beta_3 \; = \; \frac{[LH_3]}{[L][H]^3} \tag{2.11}$$

$$\vdots \qquad\qquad\qquad \vdots$$

$$\beta_n \; = \; \frac{[LH_n]}{[L][H]^n} \tag{2.12}$$

$$L \; + \; nH \; \rightleftharpoons \; LH_n \quad :$$
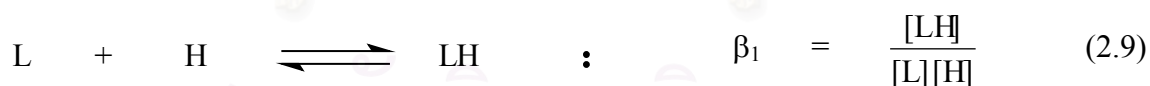
The K_n's are called the stepwise protonation constants and the β_n's are called the overall or cumulative protonation constants.

2.2.2 Stability Costants

The thermodynamic stability of complex equilibria can be characterized by stability constant and instability constant. Stability constant is a *n* equilibrium constant for the interaction of metal with ligand. Sometime stability constant is called as formation constant. In older literature, the inverse of stability constant is used andthis is known as in stability constant.

If the solution containing metal ions, M and ligand, L the system at equilibrium may be described by the following equations and stepwise equilibrium constants.

$$M \quad + \quad L \; \rightleftharpoons \; ML \quad : \quad K_1 \;\; = \;\; \frac{[ML]}{[M][L]} \qquad (2.13)$$

$$ML \quad + \quad L \; \rightleftharpoons \; ML_2 \quad : \quad K_2 \;\; = \;\; \frac{[ML_2]}{[ML][L]} \qquad (2.14)$$

$$ML_2 \quad + \quad L \; \rightleftharpoons \; ML_3 \quad : \quad K_3 \;\; = \;\; \frac{[ML_3]}{[ML_2][L]} \qquad (2.15)$$

$$ML_{n-1} \quad + \quad L \; \rightleftharpoons \; ML_n \quad : \quad K_n \;\; = \;\; \frac{[ML_n]}{[ML_{n-1}][L]} \qquad (2.16)$$
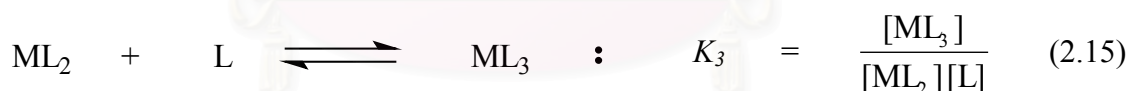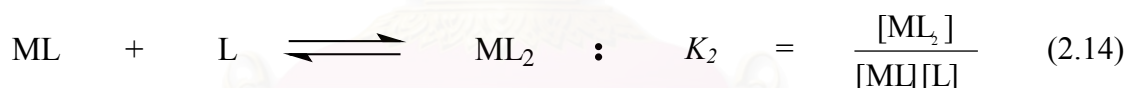
There will be n such equilibria, where n represents the maximum coordination number of the metal ion M for the ligand L. The comulative equilibrium constants can be decribed as follow:

$$M \quad + \quad L \quad \rightleftharpoons \quad ML \quad : \quad \beta_1 \quad = \quad \frac{[ML]}{[M][L]} \tag{2.17}$$

$$M \quad + \quad 2L \quad \rightleftharpoons \quad ML_2 \quad : \quad \beta_2 \quad = \quad \frac{[ML_2]}{[M][L]^2} \tag{2.18}$$

$$M \quad + \quad 3L \quad \rightleftharpoons \quad ML_3 \quad : \quad \beta_3 \quad = \quad \frac{[ML_3]}{[M][L]^3} \tag{2.19}$$

$$M \quad + \quad 4L \quad \rightleftharpoons \quad ML_n \quad : \quad \beta_n \quad = \quad \frac{[ML_n]}{[ML][L]^n} \tag{2.20}$$
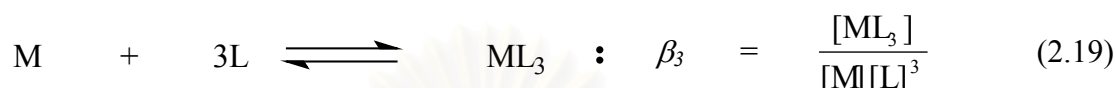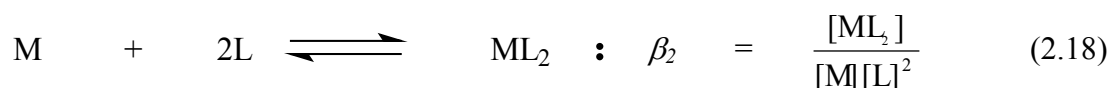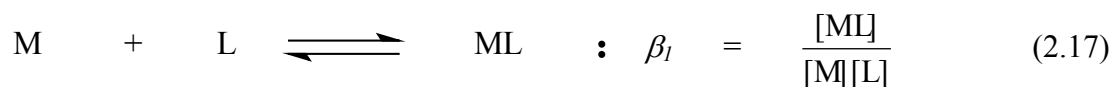
Since there can be only n independent equilibria in such a system, it is clear that the K_i's and β_i's must be related. The relationship is indeed rather obvious. Consider, for example, the expression for β_3 let us multiply both numerator and denominator by $[ML][ML_2]$ and then rearrange slightly :

$$\beta_3 \quad = \quad \frac{[ML_3]}{[M][L]^3} \cdot \frac{[ML][ML_2]}{[ML][ML_2]} \tag{2.21}$$

$$= \quad \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \frac{[ML_3]}{[ML_2][L]} \tag{2.22}$$

$$= \quad K_1 . K_2 . K_3 \tag{2.23}$$

It is not difficult to see that this kind of relationship is perfectly general, namely.

$$\beta_k \quad = \quad K_1 . K_2 ... K_k \quad = \quad \prod_{i=1}^{i=k} K_i \tag{2.24}$$

2.2.3 Secondary Concentration Variables

In order to evaluate the stability constant (K) for a simple system, in theory, it is only necessary to prepare a single solution containing a know total amount of metal

ion $[M]_T$ and ligand $[L]_T$ and measure one of the three remaining unknown concentrations. These are the free metal ion concentration $[M]$, the free ligand concentration $[L]$ and the tal-ligand complex concentration $[ML]$.

In order to evaluate these stability constants, it is necessary to find a relationship between them and the experimentally determined variables ($[M]$, $[L]$, $[H]$ etc.) This relationship is often established via the definition of secondary concentration variables. It is from these variables that the stability constants are calculated.

2.2.3.1 The protonation formation function ($\overline{P}$)

Protonation equilibria of a ligand **L** interacting in a solution of constant ionic strength can be written as follow :

$$L \quad + \quad H \quad \rightleftharpoons \quad LH \quad : \quad K_1 \quad = \quad \frac{[LH]}{[L][H]} \tag{2.25}$$

$$LH \quad + \quad H \quad \rightleftharpoons \quad LH_2 \quad : \quad K_2 \quad = \quad \frac{[LH_2]}{[LH][H]} \tag{2.26}$$

$$LH_{n-1} \quad + \quad H \quad \rightleftharpoons \quad LH_n \quad : \quad K_n \quad = \quad \frac{[LH_n]}{[LH_{n-1}][H]} \tag{2.27}$$

When n is a number of the proton bind to the ligand L. The mass balance equations for the total concentration of the ligand and proton can be written below.

$$[L]_T \quad = \quad [L] + [LH] + [LH_2] + \ldots + [LH_n] \tag{2.28}$$

$$[H]_T \quad = \quad [H] + [LH] + 2[LH_2] + \ldots + [LH_n] \tag{2.29}$$

A function p defined as the average number of proton **H** bing to the ligand **L** :

$$\overline{P} \quad = \quad \frac{\text{total bond proton}}{\text{total ligand}} \quad = \quad \frac{[H^+]_T - [H^+] + [OH^-]}{[L]_T} \tag{2.30}$$

when $[H^+]$ is concentration of the free proton obtained from the measuremant. $[OH^-]$ is the concentration due to the titrant which can be converted to $[H^+]$ via the relation of the autoprotolysis constant of methanol. The relationship between the $\overline{P}$ and the increasing of proton, as $\log [H^+]$, should illstrate the curve as shown in Figure 2.1.
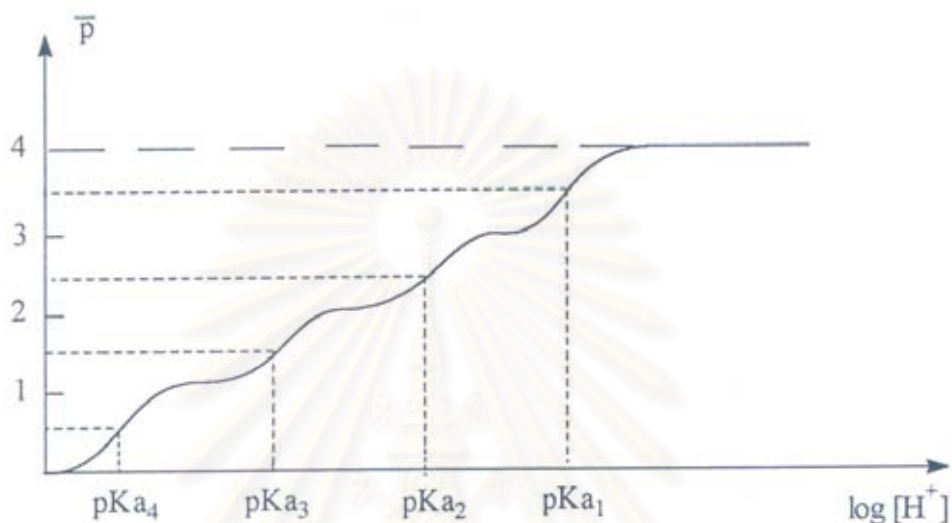
Figure 2.1   Plot of the protonation formation function ($\overline{p}$, against the logarithm of the free proton concentration ($\log [H^+]$) for tetraacid.

2.2.1.2 The complex formation function ($\overline{n}$)

Let us consider a metal ion **M** and a ligand **L** interacting in solution of constantionic strength. The equilibria present are:

$$M \quad + \quad L \quad \rightleftharpoons \quad ML \quad : \quad K_1 \quad = \quad \frac{[ML]}{[M][L]} \qquad (2.31)$$

$$ML \quad + \quad L \quad \rightleftharpoons \quad ML_2 \quad : \quad K_2 \quad = \quad \frac{[ML_2]}{[ML][L]} \qquad (2.32)$$

$$ML_{n-1} \quad + \quad L \quad \rightleftharpoons \quad ML_n \quad : \quad K_n \quad = \quad \frac{[ML_n]}{[ML_{n-1}][L]} \qquad (2.33)$$
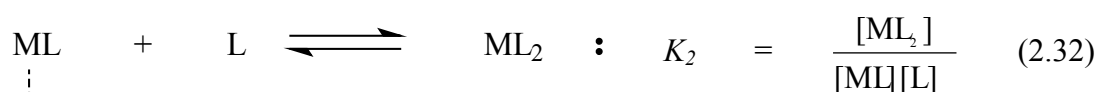
The maximum value of n, written N, will be a function of both the maximum coordination number of the netal ion and the multidentate nature of the ligand. We can now write mass balance equations for both the total metal ion and total ligand concentrations.

$$[M]_T \ = \ [M] + [ML] + [ML_2] + \ldots + [ML_n] \tag{2.34}$$

$$[L]_T \ = \ [L] + [ML] + 2[ML_2] + \ldots + n[ML_n] \tag{2.35}$$

A function $\bar{n}$ defined as the average number of ligands **L** attached to the metal **M** may be written

$$\bar{n} \ = \ \frac{\text{total bond ligand}}{\text{total metal}} \ = \ \frac{[L]_T - [L]}{[M]_T} \tag{2.36}$$

Substituting equations (2.34) and (2.35) in (2.36) yields

$$\bar{n} \ = \ \frac{[ML] + 2[ML_2] + \ldots + n[ML_n]}{[M] + [ML] + [ML_2] + \ldots + [ML_n]} \tag{2.37}$$

In summation terms equation (2.37) becomes

$$\bar{n} \ = \ \frac{\sum_{n=1}^{n=N} n[ML_n]}{[M] + \sum_{n=1}^{n=N} n[ML_n]} \tag{2.38}$$

where N is the maximum coordination number for the metal if L is a monodentate ligand. However K_n and β_n are defined by

$$K_n \ = \ \frac{[ML_n]}{[ML_{n-1}][L]} \tag{2.39}$$

$$\beta_n \ = \ \frac{[ML_n]}{[M][L]^n} \tag{2.40}$$

In addition, $\beta_n = K_1 K_2 K_3 \dots K_n$ (2.41)

and on substituting equation (2.39) into (2.37) gives

$$\bar{n} = \frac{K_1[M][L] + 2K_1K_2[M][L]^2 + \dots + nK_1K_2 \dots K_n[ML_n]}{[M] + K_1[M][L] + K_1K_2[M][L]^2 + \dots + K_1K_2 \dots K_n[M][L]^n}$$ (2.42)

and after dividing through by [M] and remembering equation (2.41)

$$\bar{n} = \frac{\beta_1[L] + 2\beta_1[L]^2 + \dots + n\beta_n[L]^n}{1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n}$$ (2.43)

which may be more conveiently written in summation terms

$$\bar{n} = \frac{\sum_{n=1}^{n=N} n\,\beta_n[L]^n}{1 + \sum_{n=1}^{n=N} \beta_n[L]^n} \equiv \frac{\sum_{n=1}^{n=N} n\,\beta_n[L]^n}{\sum_{n=0}^{n=N} \beta_n[L]^n}$$ (2.44)

It is immediately apparent from Equation (2.44) That n is solely dependent on the free ligand concentration, [L], and is independent of $[M]_T$, $[L]_T$ and the free metal ion concentration [M]. The complex formation function, $\bar{n}$ is the starting point for many of the methods used in the calculation of stability constants.

2.2.1.3 The degree of formation (α_c)

For any individual component of the system , a variable α_c can be defined such that

$$\alpha_c = \frac{[ML_c]}{[M]_T} \qquad \text{for c = 0, 1, 2, \dots N}$$ (2.45)

This variable α_c is partial mole fraction of the component ML_c. The degree of formation of the system as a whole may be considered, and another variable α_t can be defined

$$\alpha_T \quad = \quad \sum_{c=1}^{c=N} \alpha_c \tag{2.46}$$

where α_t is the fraction of total metal bound to ligand in the form of a complex. By an analogous procedure to that used to derive equation (2.44) , we can write α_c in summation terms

$$\bar{n} \quad = \quad \frac{\sum_{c=1}^{c=N} \beta_c [L]^c}{1 + \sum_{c=1}^{c=N} \beta_c [L]^c} \quad \equiv \quad \frac{\sum_{c=1}^{c=N} \beta_c [L]^c}{\sum_{c=0}^{c=N} \beta_c [L]^c} \tag{2.47}$$

One interesting solution to equation (2.45) is when c=0 and hence

$$\alpha_0 \quad = \quad \frac{[M]}{[M]_T} \tag{2.48}$$

This function, α_0 gives the species distribution for the free metal ion in the solution. When no complex formation takes place then α_0 is unity because $[M]_T = [M]$. Hence it is possible to plot a series of the component distribution curves of α_c versus $[M]_T$ or $[L]_T$. The α_c function is used to used to show at a glance the relative proportions of each of the species present in solution.

2.2.2.4 The degree of complex formation (ϕ)

A third secondary concentration variable $\emptyset$ is defined as:

$$\phi \quad = \quad \frac{[M]}{[M]_T} \quad = \quad 1 + \sum_{n=1}^{n=N} \beta_n [L]^n \tag{2.49}$$

At this stage it is valuable to summarize the definitions of three secondary concentration variables that we have met so far. This, together with experimental data that must be available to use each of them, is given in Table 2.2

Table 2.2   Summary of the secondary concentration variables

Variable	Title	Definition	Experimental Observable required
$\bar{n}$	Complex formation function	$([L]_T - [L]) / [M]_T$	$([L]_T - [L]) / [M]_T$
α_c	Degree of formation	$[ML]_c / [M]_T$	$[M]_T , [L]_T , [L]$
$\varnothing$	Degree of the complex Formation	$[M]_T / [M]$	$[M]_T , [M]$

2.3   Computation of Equilibrium Constants by SUPERQUAD Programme

The computer programme, SUPERQUAD[18] has been widely used to calculate stability constants o species in solution equilibria from data obtained by potentiometric method. The formation constants are determined by minimization of an error-square sum based on measure electrode potentials. The programme also permits refinement of any reactant concentration or standard electrode potential.   The refinement is incorporated in to new procedure which can be used for model selection.   The assumptions for computation of formation constants by SUPERQUAD could be described as follows.

Assumptions   :   There are number of assumptions underlying the whole treatment, and each needs to be considered explicitly.

1. For each chemical species $A_aB_b\ldots$ in the solution equilibria, there is a chemical constant, the formation constant, which is expressed as a concentration quotient in equation (2.50)

$$\beta_{ab\cdots} = \frac{[A_aB_b\ldots]}{[A]^a[B]^b\ldots} \qquad (2.50)$$

A, B… are the reactants (SUPERQUAD allows up to four of them) and [A], [B] are the concentrations of free reactant; electrical charges may be attached to any species,but they are omitted for sake of simplicity in this discussion. Since the thermodynamic definition of a formation constant is as an activity quotient, it is to be assumed that the quotient of the activity coefficients is constant, an assumption usually justified by performing the experiments with a medium of high ionic strength.

2. Each electrode present exhibits a pseudo-Nernstian behavior, equation (2.51), where [A] is the concentration of the electro-active ion,

$$E = E^o + S_L \log [A] \qquad (2.51)$$

E is the measured potential, and E^o is the standard electrode potential. The ideal value of the slope S_L is of course RT/nF, but we assume only that it is a constant for a given electrode. The value of E^o and S_L are usually obtained in separate calibration experiment. Further there is a modified Nernst equation.

$$E = E^o + S_L \log [H^+] + r [H^+] + s [H^+]^{-1} \qquad (2.52)$$

This equation was first suggested as means of taking into account junction potentials in strongly acidic and strongly basic condition.

3. Systematic errors must be minimized by careful experimental work. Sources of systematic error include electrode calibration, sample weighings and   dilutions, standardization of reagents (use of carbonate-free alkali in particular), temperature variation and water quality. The last-named factor is more significant today than it was in the past, as water may be contaminated by titrable species which can pass through distillation columns by surface action. All statistical tests are based on the assumption that systematic errors are absent from the data.

4. The independent variable is not subject to error. Errors in the dependent variable are assumed to have a normal distribution. If these assumptions are true use of the principle of least squares will yield a maximum likelihood result, and computed residuals should not show systematic treands.

5. There exits a model of the equilibrium system, which adequately accounts for the experimental observations. The nodel is specified by a set of coefficients a, b, …, one for each species formed. All least-squares refinements are performed in tems of an assumed model. Examination of a sequence of models shoukd yield a best model which is not significantly different from the true model. Choice of the best model is know as species selection.

2.4   Equilibrium Constants by UV Spectrometry

UV spectrometry is a complementary method to potentiometry. UV spectrometry can be applied for formation study, at least product and reactance of reacting species in equilibrium must absorb UV light. The fundamental law of absorption in spectrometry is the Beer-Lambert-Bouguer law, commonly called Beer's law.

2.4.1 Beer-Lambert-Bouguer Law

The beer's law defines the intensity of any particular absorption band (A) in terms of the molar absorptivity ε, as following equation.

$$A = \varepsilon \, c \, l \tag{2.53}$$

Where c and l are concentration usually in molar and path length in cm, respectively. Observed absorbance of n species at wavelength λ per unit path length of any soluiton, A_{obs}^{λ} may be expressed as a function of molar absorptivity at the same wavelength by equation below.

$$A_{obs}^{\lambda} = \varepsilon_1^{\lambda} c_1 + \varepsilon_2^{\lambda} c_2 + \dots \varepsilon_n^{\lambda} c_n \tag{2.54}$$

where ε_1^{λ}, ε_2^{λ}, ε_n^{λ} are the molar absorptivities of species 1, 2 and n at wavelength λ. For c_1, c_2 and c_n are their respective concentrations.

2.4.2 Calculation of Stability Constants from Spectrometric Data

Let consider a metal ion, M and a ligand, L interacting in a solution of constant ionic strenth. The equilibria present are :

$$M \quad + \quad L \quad \underset{\xleftarrow{\hspace{1cm}}}{\overset{K_1}{\xrightarrow{\hspace{1cm}}}} \quad ML \tag{2.55}$$

$$ML \quad + \quad L \quad \underset{\xleftarrow{\hspace{1cm}}}{\overset{K_2}{\xrightarrow{\hspace{1cm}}}} \quad ML_2 \tag{2.56}$$

$$ML_{n-1} \quad + \quad L \quad \underset{\xleftarrow{\hspace{1cm}}}{\overset{K_n}{\xrightarrow{\hspace{1cm}}}} \quad ML_n \tag{2.57}$$

Due to mass balance equations, the total metal ion and ligand concentrations can be written as

$$[M]_T = [M] + [ML] + [ML_2] + \dots [ML_n] \tag{2.58}$$

$$[L]_T = [L] + [ML] + 2[ML_2] + \ldots n[ML_n] \qquad (2.59)$$

A function $\bar{n}$, defined as the average number of lignads L attached to the metal M can be written

$$\bar{n} = \frac{\text{total bound ligand}}{\text{total metal}} = \frac{[L]_T - [L]}{[M]_T} \qquad (2.60)$$

Substituting Equation (2.58) and (2.59) in (2.60) yields

$$\bar{n} = \frac{[ML] + 2[ML_2] + \ldots n[ML_n]}{[M] + [ML] + [ML_2] + \ldots [ML_n]} \qquad (2.61)$$

In summation terms equation (2.61) becomes

$$\bar{n} = \frac{\sum\limits_{i=1}^{i=n} i[ML_i]}{[M] + \sum\limits_{i=1}^{i=n} [ML_i]} \qquad (2.62)$$

K_n and β_n are stepwise and overall stability constants as defined by

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \qquad (2.63)$$

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \qquad (2.64)$$

Combining equation (2.64) into (2.68) gives

$$\bar{n} = \frac{\sum\limits_{i=1}^{i=n} i\,\beta_i[L]^i}{1 + \sum\limits_{i=1}^{i=n} [L]^i} \qquad (2.65)$$

Two methods for quantitative role of spectrophotometry in determining the number of species in solution are a method of continuous variations and mole ratio method.

These two methods can be extended to allow calculation of the stability constants. In principle, the studying of the formation of 1:1 complex using spectrophotometry can be defined into four possibilities.

1. The molar absorptivities of M, L and ML are known or can be determined directly.
2. The molar absorptivities of any two of M, L and ML are known.
3. The molar absorptivities of only one of M, L and ML is known.
4. The molar absorptivities of none of the species is known.

For the systems with multicomplex formation, which are the most common, computational method are usually used to determine the molar absorptivities.

2.4.3 Method of Corresponding Solutions

This method can be used to overcome the problem of unknown and often unwanted molar absorptivities when using spectrophotometric data to determine stability constants. An equilibrium system of the solution of existing species L, M, ML, ML$_2$, … ML$_i$ … and ML$_n$ is considered. A function $\varepsilon_{obs}^\lambda$, can be defined as

$$\varepsilon_{obs}^\lambda = \frac{A_{obs}^\lambda - \varepsilon_L^\lambda [L]_T}{[M]_T} \qquad (2.66)$$

Where $[L]_T$ and $[M]_T$ are total concentration of L and M respectively. Therefore, the absorbance A_{obs}^λ can be written as

$$A_{obs}^\lambda = \varepsilon_M^\lambda [M] + \sum_{i=1}^{i=n} (\varepsilon_i^\lambda [ML_i]) + \varepsilon_L^\lambda [L] \qquad (2.67)$$

Where ε_M^λ, ε_L^λ and ε_i^λ are the molar absorptivities of the metal, ligand and complexes ML$_i$ at wavelength λ. Substituting (2.67) in (2.66) gives,

$$\varepsilon_{obs}^\lambda = \frac{\varepsilon_M^\lambda [M] + \sum_{i=1}^{i=n} (\varepsilon_i^\lambda [ML_i]) - \varepsilon_L^\lambda ([L]_T - [L])}{[M]_T} \qquad (2.68)$$

and from equation (2.59),

$$\varepsilon_{obs}^{\lambda} = \frac{\varepsilon_{M}^{\lambda}[M] + \sum\limits_{i=1}^{i=n}(\varepsilon_{i}^{\lambda}[ML_i]) - \sum\limits_{i=1}^{i=n}(\varepsilon_{L}^{\lambda} i [ML_i]^{i})}{[M]_T} \qquad (2.69)$$

Substituting , equation (2.64) to (2.69) gives

$$\varepsilon_{obs}^{\lambda} = \frac{\varepsilon_{M}^{\lambda}[M] + \sum\limits_{i=1}^{i=n}(\varepsilon_{i}^{\lambda}\beta_i[M][L]^{i} - i\varepsilon_{L}^{\lambda}\beta_i[M][L]^{i})}{[M]_T} \qquad (2.70)$$

Dividing through by [M] results

$$\varepsilon_{obs}^{\lambda} = \frac{\varepsilon_{M}^{\lambda} + \sum\limits_{i=1}^{i=n}(\varepsilon_{i}^{\lambda} - i\varepsilon_{L}^{\lambda})\beta_i[L]^{i}}{[M]_T / [M]}$$

(2.71)

From equation (2.58) and (2.64)

$$\varepsilon_{obs}^{\lambda} = \frac{\varepsilon_{M}^{\lambda} + \sum\limits_{i=1}^{i=n}(\varepsilon_{i}^{\lambda} - i\varepsilon_{L}^{\lambda})\beta_i[L]^{i}}{1 + \sum\limits_{i=1}^{i=n}\beta_i[L]^{i}}$$

(2.72)

Hence $\varepsilon_{obs}^{\lambda}$ is a function of [L] and it can be calculated from the absorbances of solutions of different $[L]_T$ and $[M]_T$ values using equation (2.70). It follows that solutions having the same value of $\varepsilon_{obs}^{\lambda}$ must have the same value for [L]. Since $\bar{n}$ is a function of [L] only, it also follows that these solutions have the same value of $\bar{n}$.

From Equation (2.60),

$$[L]_T = [L] + \bar{n}[M]_T \qquad (2.73)$$

and for a constant value of [L] this is a linear equation whose slope is and intercept [L].
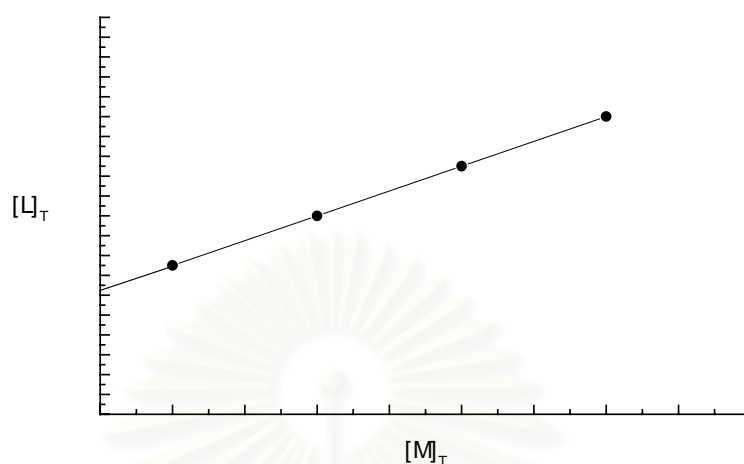
Figure 2.2 Corresponding solution of $[L]_T$ against $[M]_T$ for a series of solutions having the same value of $\varepsilon_{obs}^{\lambda}$

2.5   Inert Background Electrolyte

The study acid-base characteristics of ligand and their complexation properties toward metal, ionic strength will be controlled by inert background electrolyte present at a concentration far in excess that of the reacting ionic species under investigation. Inert Background electrolyte is sometime called inert background solution or supporting electrolyte which is defined as eletrolyte which does not react with any of reacting species such as metal ion, ligand or metal-ligand species in the equilibrium being studied. The main function of the inert background electrolyte to keep theoverall ionic strength and activity coefficient constant. Properties of the chosen inert background eletrolyte must meet the following requirements

(1)   a strong and non reacting (inert) electrolyte,

(2)   no part of electrolyte involved in equilibrium under investigation,

(3)   its cation must not associate with the ligand with the complex species,

(4)   its anion must not associate with the central metal ion and with the complex species,

(5)   redox reaction must not occur between the constituents of the inert electrolyte and the central ion or ligand,

(6)   its solubility has to be large enough,

(7)   its contribution to the measured physical or chemical property must be negligible.

Common background electrolytes used in the methanolic solutions are tetraethylammonium perchlorate (Et_4NCIO_4), and tetramethylammonium chloride (Me_4NCI). The Me_4NCI is not suitable for investigating the complex formation in the methanolic solution because chloride ions can form complexes with many transition metal ions,

The tetrabutylammonium trifluoromethanesulfonate ($Bu_4NCF_3SO_3$)   was recently introduced to be used as the inert background electrolyte in methanol[19]. The $Bu_4NCF_3SO_3$ was examined for being used as the inert background in methanolic solution in order to avoid the use of explosive substance such as perchlorate salts.

2.6   Quantum Chemical Calculation

2.6.1   Basis Set Effects

A basis set is the mathematical description of the orbitals within a system which in turn combine to approximate the total electronic wavefunction, used to perform the theoretical calculation. Larger basis sets more accurately approximate the orbitals by imposing fewer restrictions on the locations of the electrons in space. In the true quantum mechanical picture, electrons have affinite probability of existing anywhere in space; this limit corresponds to the infinite basis set expansion.

Standard basis sets for electronic structure calculations use linear combinations of gaussian functions to form the orbitals. Gaussian program offers a wide range of pre-defined basis sets, which may be classified by the number and types of basis functions that they contain. Basis sets assign a group of basis functions to each atom within a molecule to approximate its orbitals. These basis functions themselves are composed of a linear combination of gaussian functions; such basis functions are referred to as

contracted functions, and the component gaussian functions are referred to as primitives. A basis function consisting of a single gaussian function is termed uncontracted.

2.6.1.1 Minimal Basis Sets

Minimal basis sets contain the minimum number of basis functions needed for each atom, as in these examples:

$$H : 1s$$
$$C : 1s, 2s, 2p_x, 2p_y, 2p_z$$
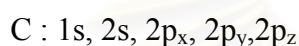
Minimal basis sets use fixed-size atomic-type orbitals. The STO-3G basis set[20] is a minimal basis set (although it is not the smallest possible basis set). It uses three gaussian primitives per basis function, which accounts for the "3G" in its name. "STO" stands for "Slater-type orbitals" and the STO-3 basis set approximates Slater orbitals with gaussian functions.

2.6.1.2 Split Valence Basis Sets

The first way that a basis set can be made larger is to increase the number of basis functions per atom. Split valence basis sets, such as 6-31G[21-25], have two or more sizes of basis function for each valence orbital. For example, hydrogen and carbon are represented as:

$$H : 1s, 1s'$$
$$C : 1s, 2s, 2s', 2p_x, 2p_x', 2p_y, 2p_y', 2p_z, 2p_z'$$
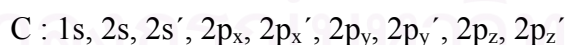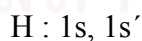
Where the primed and umprimed orbitals differ in size.

The double zeta basis sets, such as the Dunning-Huzinage basis set[26] (D95), form all molecular orbitals from linear combinations of two sizes of functions for each atomic orbital. Similarly, triple split valence basis sets, like 6-311G[27-33], use three sizes of contracted functions for each orbital-type.

2.6.2   Practical considerations when performing *ab inito* calculations

Ab inito calculations can be extremely time-consuming, especially when using the higher levels of theory or when the nuclei are free to move, as in a minimization calculation. Various "tricks" have been developed which can significantly reduce the computational effort involved. Many of these options are routinely available in the major software packages and are invoked by the specification of simple keywords. One common tactic is to combine different levels of theory for the various stages of a calculation. For example, a lower level of theory can be used to provide the initial guess for the density matrix prior to the first SCF iteration. Lower levels of theory can also be used in other ways. Suppose we wish to determine some of the electronic properties of a molecule in a minimum energy structure. Energy minimization requires that the nuclei move, and is typically performed in a series of steps, at each of which the energy (and frequently the gradient of the energy) must be calculated. Minimization is therefore a computationally expensive procedure, particularly when performed at the high level of theory. To reduce this computational burden a lower level of theory can be employed for the geometry optimization. A "single point" calculation using a high level of theory is then performed at the geometry so obtained to give a wavefunction from which the properties are determined. The assumption here of course is that the geometry does not change much between the two levels of theory. Such calculations are denoted by slashes (/). For example, a calculation that is described as "6-31G*/STO-3G" indicates that the geometry was determined using the STO-3G basis set and the wavefunction was obtained using the 6-31G* basis set. Two slashes are used when each calculation is itself described using a slash, such as when electron correlation methods are used. For example, "MP2/6-31G*//HF/6-31G*" indicates a geometry optimization using a Hartree-Fock calculation with a 6-31G* basis set followed by a single-point calculation using the MP2 method for incorporating electron correlation, again using a 6-31G* basis set.

2.6.3   Setting up the calculation and the choice of coordinates

The traditional way to provide the nuclear coordinates to a quantum mechanical program is via a Z-matrix, in which the positions of the nuclei are defined in terms of a

set of internal coordinates. Some programs also accept coordinates in Cartesian format, which can be more convenient for large systems. It can sometimes be important to choose an appropriate set of internal coordinates, especially when locating minima or transition points or when following reaction pathways.

2.6.4   Calculating derivatives of the energy

Considerable effort has been spent devising efficient ways of calculating the first and second derivatives of the energy with respect to the nuclear coordinates. Derivatives are primarily used during minimization procedures for finding equilibrium structures and are also used by methods, which locate transition structures and determine reaction pathways. To calculate derivatives of the energy it is necessary to calculate the derivatives of the various electron integrals. For Gaussian basis sets the derivatives can be obtained analytically, and it is relatively straightforward to obtain first derivatives for many levels of theory. The time taken to calculate the derivatives is comparable to that required for the calculation of the total energy. Second derivatives are more difficult and expensive to calculate, even at the lower levels of theory.

2.6.5 Basis set superposition error

Suppose we wish to calculate the energy of formation of a bimolecular complex, such as the energy of formation of a hydrogen-bonded water dimer. Such complexes are sometimes referred to as "supermolecules". One might expect that this energy value could be obtained by first calculating the energy of a single water molecule, then calculating the energy of the dimer, and finally subtracting the energy of the two isolated water molecules from that of the dimer. However, the energy difference obtained by such an approach will invariably be an overestimate of the true value. The discrepancy arises from a phenomenon known as basis set superposition error (BSSE). As the two water molecules approach, the energy of the system falls not only because of the favourable intermolecular interactions but also because the basis functions on each molecule provide a better description of the electronic structure around the other

molecule. It is clear that the BSSE would be expected to be particularly significant when small, inadequate basis sets are used, e.g. the minimal basis STO-nG basis sets, which do not provide for an adequate representation of the electron distribution far from the nuclei, particularly in the region where non-covalent interactions are strongest. One way to estimate the basis set superposition error is via the counterpoise correction method of Boys and Bernardi in whichtheentire basis set is included in all calculations. Thus, in the general case:

$$A + B \equiv AB$$

$$\Delta E = E(AB) - [E(A) + E(B)]$$

The calculation of the energy of the individual species A is performed in the presence of "ghost" orbitals of B; that is, without the nuclei or electrons of B. A similar calculation is performed for B using ghost orbitals on A. An alternative approach is to use a basis set in which the orbital exponents and contraction coefficients have been optimized for molecular calculations rather than for atoms. The relevance of the basis set superposition error and its dependence upon the basis set and the level of theory employed, i.e. SCF or with electron correlation, remains a subject of much research.

2.6.6   Semi-empirical Methods

2.6.6.1 AM1 (Austin Model 1) Method

AM1[34] was modified from MNDO (Modified Neglect of Diatomic Overlap) method and became clear that there were certain systematic errors. For example the repulsion between two atoms which are 2-3 Å apart is too high. This has as a consequence that activation energies in general are too large. The source was traced to too repulsive an interaction in the core-core potential. To remedy this, the core-core

function was modified by adding Gaussian functions, and the whole model was reparameterized. The core-core repulsion of AM1 has the form

$$V_{nn}(A,B) = V_{nn}^{MINDO}(A,B) + \frac{Z_A' Z_B'}{R_{AB}} x \left(\sum_k a_{kA} e^{-b_{kA}(R_{AB}-c_{kA})^2} + \sum_k a_{kB} e^{-b_{kB}(R_{AB}-c_{kB})^2} \right)$$

(2.74)

Where k is between 2 and 4 depending on the atom. It should be note that the Gaussian functions more or less were added as patches onto the underlying parameters, which explains why different number of Guassians are used for each atom. As with MINDO, the G_{ss}, G_{sp}, G_{pp}, G_{p2}, H_{sp} parameters are taken from atomic spectra, while the rest including the a_k, b_k and c_k constants, are fitted to molecular data.

2.6.6.2   PM3 Method

PM3[34] is a short name of MNDO-PM3 (Modified Neglect of Diatomic Overlap, Parametric Method Number 3). PM3 is a method of the optimization process automatic, by deriving and implementing formulas for the derivative of a suitable error function with respect to the parameters. All parameters could then be optimized simultaneously, including the two-electron terms, and a significantly larger trianing set with several hundred data could be employed.

CHAPTER III

EXPERIMENTAL

3.1 Chemical and Instruments

3.1.1 Chemicals

1.	Tetrabutylammonium trifluoromethanesulfonate	Electrochemical grade, Fluka, Switzerland
2.	Tetrabutylammonium hydroxide 0.1 M solution in 2-propanol/methanol	Analar grade, Riedel-de Haen, Germany
3.	Methylenechloride	Analar grade, Merck, Germany
4.	Potassium hydrogenphthalate	Analar grade, Carlo Erba, Italy
5.	Perchloric acid 70-72%	Analar grade, Merck, Germany
6.	Methanol	Analar grade, Merck, Germany
7.	Copper (II) trifluoromethanesulfonate	Analar grade, Aldrich, U.S.A.
8.	Zinc (II) trifluoromethanesulfonate	Analar grade, Aldrich, U.S.A.
9.	Europium (III) trifluoromethanesulfonate	Analar grade, Aldrich, U.S.A.
10.	Yttrium (III) trifluoromethanesulfonate	Analar grade, Aldrich, U.S.A.
11.	Argon gas	Ultra high purity grade
12.	Nitrogen gas	Analytical grade
13.	Calix[4]-cyclen-benzocrown-6 (L)	synthesized by the method decribed in reference 35

3.1.2 Instruments

1. Automatic titratior, Mettler, Model DL 25, Switzerland
2. Thermostat, Heto, Model DT-2, Denmark
3. Combined pH electrode, Mettler, Model DG 113-SC, Switzerland
4. UV-VIS Spectrophotometer, HP 8453
5. Magnetic Stirrer
6. Micrometer Syringe 2.00 cm^3, GS-1200, Gilmont, USA
7. Personal Computer, Pentium II/350 IBM-PC300Gl, RAM 512 MB

3.2 Potentiometric titration

3.2.1 Preparation of Solutions

Tetrabutylammonium trifluoromethanesulfonate ($Bu_4NCF_3SO_3$) was used as an inert background electrolyte for the basicity study of calix[4]-cyclen-benzocrown-6 (**L**). The solution of the inert background electrolyte solution, 1.00×10^{-2} M $Bu_4NCF_3SO_3$ was prepared by dissolution of a weighted quantity of dried $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH. The solution of 1.00×10^{-2} M tetrabutylammonium hydroxide (Bu_4NOH) was used as titrant base. The primary standard solution of potassium hydrogen phthalate (KHP) was prepared by dissolution of a weighed quantity of potassium hydrogen phthalate (KHP) in water and used for standardization of tetrabutylammonium hydroxide (Bu_4NOH) solution. The stock solution of perchloric acid ($HClO_4$) was made by dilution of the commercial concentrated solution (70-72% in water) in 40% CH_2Cl_2/CH_3OH. The perchloric standard solution of pH = 2 (1.00×10^{-2} M $HClO_4$) and pH = 3 (1.00×10^{-3} M $HClO_4$) in the inert background electrolyte solution were prepared from stock solution of perchloric acid ($HClO_4$) and used for electrode calibration. All solutions of the perchloric standard solution were standardized with the tetrabutylammonium hydroxide (Bu_4NOH) solution prior to use. The solutions of calix [4]-cyclen-benzocrown-6 (**L**) were prepared by dissolving weighted quantities of ligand **L** in the inert background electrolyte solution.

3.2.2   The Calibration of Electrode

For the basicity study of calix[4]-cyclen-benzocrown-6 (**L**), all titrations were carried out at 25°C under argon atmosphere saturated with 1.00×10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH solution. The electrode was calibrated at pH = 2 with the pH standard solution of pH = 2 (1.00×10^{-2} M $HClO_4$ in the presence of 1.00×10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH) by adjustment of the Nernstian slope as defined the ratio between pH and potential in units of millivolt based on the isopotential point of pH $8.30 = 0.0$ millivolt, As the junction potentials of electrode vary exponentially with $-\log[H^+]$, the pH of solution can be corrected by using the following equation.

$$pH_{corrected} = pH_{observed} + a + b \, [H^+]_{observed}$$

The constants a and b were determined from a measurement of the pH standard solution of pH = 3 (1.00×10^{-2} M $HClO_4$ in the presence of 1.00×10^{-3} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH. Both a and b value were includes to the treatment program in order to obtain the accurate pH value.

3.2.3 Potentiometric Titrations

For the basicity study of calix[4]-cyclen-benzocrown-6 (**L**) in 1.00 x 10^{-2} M Bu$_4$NCF$_3$SO$_3$ in 40% CH$_2$Cl$_2$/CH$_3$OH have been studied by potentiometric titration. For typically 10 mL of the ligand solution was add to various amount of 1.00 x 10^{-2} M HClO$_4$ in the presence of 1.00 x 10^{-2} M Bu$_4$NCF$_3$SO$_3$ in 40% CH$_2$Cl$_2$/CH$_3$OH to obtain various ratio of ligand to proton. Each solution was titrated with the 1.00 x 10^{-2} M tetrabutylammonium hydroxide (Bu$_4$NOH) solution and the experimental data used in computer simulations for determining the proton constants are shown in Table 3.1. The pH of solution was adjusted by 1.00 x 10^{-2} M HClO$_4$ in the presence of 1.00 x 10^{-2} M Bu$_4$NCF$_3$SO$_3$ in 40% CH$_2$Cl$_2$/CH$_3$OH. Each solution was titrated with the 1.00 x 10^{-2} M tetrabutylammonium hydroxide (Bu$_4$NOH) solution and the experimental data used in computer simulations for determining the proton constants are shown in Table 3.1.

Table 3.1 Experimental data used in computer simulations for determing the protonation constants of calix[4]-cyclen-benzocrown-6 (**L**) in 1.00 X 10^{-2} M Bu$_4$NCF$_3$SO$_3$ in 40% CH$_2$Cl$_2$/CH$_3$OH, at 25°C.

Titration	Initial concentration (mM)		pH range	Data points
	L	**Proton**		
1	0.910	1.199	2.86-10.97	56
2	0.900	2.180	2.71-10.64	71
3	0.970	3.285	2.66-9.78	70

3.3 UV-VIS spectrophotometric Titration

3.3.1 Preparation of Solutions

The solution of calix[4]-cyclen-benzocrown-6, **L** was prepared by dissolving weighted quantities of ligand **L** in 1.00×10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH. The solutions of transition metal ions Cu^{2+}, Zn^{2+}, Eu^{3+} and Y^{3+} were prepared by dissolution of the weighed quantity of $Cu(CF_3SO_3)_2$, $Zn(CF_3SO_3)_2$, $Eu(CF_3SO_3)_3$ and $Y(CF_3SO_3)_3$ in 1.00×10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH.

3.3.2 UV-VIS Spectrophotometric Titration

As titrand, 3.00 cm^3 of ligand L in 1.00×10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH solution was placed in UV-VIS titrating cell (cuvet size ca. 4 cm^3). UV-VIS Spectrophotometric titrations were recorded against the supporting electrolyte (1×10^{-2} M $Bu_4NCF_3SO_3$). The titrations were performed at room temperature, ca. 25 °C. Solution was stired ca. 3 minutes using a magnetic stirer before recording its spectra.

Metal ion solution was added 0.05 cm^3 for each titation step from a micrometer syringe of size 2.00 cm^3, GS-1200, Gilmont (connected with capillary teflon tube). Each system, at least ten titration steps were performed. Using the wavelength between 200 to 400 nm, the absorbance of each solution was measured.

3.3.3 Treatment of UV-VIS Spectrophotometric Data

Absorbances were seleceted from the whole range of UV-VIS spectra. The absorbances at selected wavelengths steping by 10 to 20 nm were collected for at least ten different numbers of wavelength. The stability constants of complexes between ligand and metal ions were calculated from the collecting data. The evaluation processes were performed on the SIRKO computer program.[36] The selected UV-VIS spectral data of titration system for ligand complexing with Cu(II), Zn(II), Eu(III) and Y(III) ions are shown in Tables 3.2, 3.3, 3.4 and 3.5, respectively.

Table 3.2(a) Selected UV-VIS spectrophotometric titration data of ligand **:**Cu(II) system with metal to ligand ratio varied from 0.1 to 1, $C_{initial}$ of ligand and Cu(II) are 1.0×10^{-5} and 6.0×10^{-5} M, $V_{initial}$ is 3.00 cm^3.

Volume	Wavelength (nm)								
(cm^3)	200	210	220	230	240	250	260	270	280
0.00	0.0153	0.1164	0.1372	0.5099	0.0458	0.0020	0.0071	0.0361	0.0360
0.05	0.0514	0.0853	0.1293	0.5007	0.0461	0.0043	0.0100	0.0391	0.0385
0.10	0.0586	0.1067	0.1349	0.5007	0.0522	0.0108	0.0164	0.0448	0.0438
0.15	0.0619	0.1036	0.1339	0.4986	0.0528	0.0121	0.0181	0.0467	0.0456
0.20	0.0276	0.1283	0.1357	0.4929	0.0541	0.0147	0.0213	0.0497	0.0482
0.25	0.0350	0.1047	0.1410	0.4876	0.0552	0.0166	0.0234	0.0517	0.0503
0.30	0.0560	0.1336	0.1319	0.4760	0.0517	0.0144	0.0218	0.0501	0.0488
0.35	0.0496	0.1098	0.1368	0.4697	0.0522	0.0157	0.0233	0.0518	0.0506
0.40	0.1235	0.0980	0.1395	0.4664	0.0542	0.0190	0.0268	0.0547	0.0532
0.45	0.0704	0.0983	0.1408	0.4566	0.0522	0.0182	0.0266	0.0546	0.0530
0.50	0.0838	0.0976	0.1287	0.4524	0.0540	0.0209	0.0296	0.0573	0.0558
$\varepsilon_L{}^a$	5.8623	10.6678	13.4865	50.0653	5.2173	1.0825	1.6435	4.4764	4.3838

[a] Molar absorptivities calculated from A_L/C_L in mM^{-1}cm^{-1}.

Table 3.2 (b) Selected UV-VIS spectrophotometric titration data of ligand **:**Cu(II) system with metal to ligand ratio varied from 1 to 11, $C_{initial}$ of ligand and Cu(II) are 5.0×10^{-6} and 3.0×10^{-4} M, $V_{initial}$ is 3.00 cm^3.

Volume	Wavelength (nm)										
(cm3)	220	230	240	250	260	270	280	290	300	310	320
0.05	0.1054	0.2467	0.0489	0.0371	0.0481	0.0694	0.0704	0.0359	0.0284	0.0266	0.0250
0.10	0.1075	0.2393	0.0527	0.0463	0.0617	0.0848	0.0844	0.0460	0.0337	0.0282	0.0252
0.15	0.1057	0.2387	0.0586	0.0562	0.0752	0.1001	0.0986	0.0563	0.0391	0.0300	0.0258
0.20	0.1153	0.2367	0.0632	0.0650	0.0877	0.1143	0.1116	0.0658	0.0437	0.0314	0.0258
0.25	0.1085	0.2358	0.0683	0.0737	0.1003	0.1287	0.1248	0.0756	0.0489	0.0333	0.0266
0.30	0.1168	0.2322	0.0725	0.0823	0.1124	0.1424	0.1375	0.0847	0.0537	0.0349	0.0269
0.35	0.1287	0.2295	0.0771	0.0911	0.1249	0.1567	0.1508	0.0948	0.0595	0.0378	0.0287
0.40	0.1277	0.2299	0.0836	0.1011	0.1383	0.1717	0.1645	0.1049	0.0650	0.0401	0.0297
0.45	0.1287	0.2275	0.0858	0.1070	0.1476	0.1823	0.1739	0.1111	0.0671	0.0393	0.0275
0.50	0.1407	0.2304	0.0924	0.1168	0.1608	0.1970	0.1877	0.1221	0.0743	0.0436	0.0309
0.55	0.1473	0.2310	0.0976	0.1253	0.1721	0.2098	0.1995	0.1308	0.0791	0.0455	0.0318
$\varepsilon_L{}^a$	10.5416	24.6669	4.8852	3.7145	4.8130	6.9406	7.0389	3.5866	2.8404	2.6563	2.5010

[a] Molar absorptivities calculated from A_L/C_L in mM^{-1}cm^{-1}.

Table 3.3 (a) Selected UV-VIS spectrophotometric titration data of ligand **:**Zn(II) system with metal to ligand ratio varied from 1 to 11, $C_{initial}$ of ligand and Zn(II) are 2.0×10^{-5} and 1.2×10^{-3} M, $V_{initial}$ is 3.00 cm^3.

Volume	Wave length (nm)									
(cm^3)	220	230	240	250	260	270	280	290	300	310
0.05	0.2080	0.8170	0.0885	0.0477	0.0908	0.1705	0.1773	0.0513	0.0147	0.0094
0.10	0.2139	0.8021	0.0864	0.0464	0.0890	0.1676	0.1746	0.0508	0.0147	0.0097
0.15	0.2156	0.7906	0.0854	0.0460	0.0881	0.1658	0.1728	0.0507	0.0147	0.0099
0.20	0.2134	0.7773	0.0826	0.0443	0.0860	0.1628	0.1700	0.0499	0.0143	0.0094
0.25	0.2066	0.7656	0.0815	0.0438	0.0848	0.1607	0.1681	0.0497	0.0143	0.0095
0.30	0.2014	0.7544	0.0804	0.0436	0.0844	0.1594	0.1668	0.0502	0.0151	0.0103
0.35	0.1981	0.7416	0.0778	0.0417	0.0820	0.1560	0.1638	0.0486	0.0137	0.0091
0.40	0.1962	0.7324	0.0784	0.0429	0.0828	0.1560	0.1638	0.0501	0.0155	0.0108
0.45	0.1994	0.7209	0.0754	0.0405	0.0801	0.1525	0.1603	0.0482	0.0136	0.0090
0.50	0.2028	0.7107	0.0743	0.0401	0.0792	0.1509	0.1590	0.0483	0.0142	0.0097
0.55	0.1924	0.6993	0.0720	0.0385	0.0771	0.1479	0.1559	0.0470	0.0132	0.0087
0.60	0.1946	0.6906	0.0720	0.0392	0.0774	0.1472	0.1553	0.0480	0.0145	0.0101
0.65	0.1917	0.6808	0.0701	0.0376	0.0755	0.1446	0.1528	0.0468	0.0136	0.0092
$\varepsilon_L{}^a$	10.4021	40.8499	4.4257	2.3826	4.5402	8.5255	8.8628	2.5670	0.7350	0.4709

[a] Molar absorptivities calculated from A_L/C_L in mM^{-1}cm^{-1}.

Table 3.3 (b)Selected UV-VIS spectrophotometric titration data of ligand **:**Zn(II) system with metal to ligand ratio varied from 10 to 110, $C_{initial}$ of ligand and Zn(II) are 2.0 x 10^{-5} and 1.2 x10^{-2} M, $V_{initial}$ is 3.00 cm^3.

Volume	Wave length (nm)													
(cm^3)	220	230	240	250	260	270	280	290	300	310	320	330	340	350
0.05	0.2404	0.7716	0.1090	0.0706	0.1063	0.1744	0.1714	0.0525	0.0255	0.0183	0.0135	0.0104	0.0092	0.0089
0.10	0.2476	0.7618	0.1101	0.0734	0.1093	0.1774	0.1745	0.0554	0.0280	0.0209	0.0161	0.0130	0.0119	0.0114
0.15	0.2362	0.7536	0.1116	0.0758	0.1116	0.1791	0.1765	0.0588	0.0306	0.0235	0.0188	0.0157	0.0144	0.0138
0.20	0.2365	0.7418	0.1102	0.0756	0.1110	0.1777	0.1754	0.0587	0.0306	0.0235	0.0188	0.0156	0.0143	0.0139
0.25	0.2401	0.7322	0.1097	0.0756	0.1106	0.1763	0.1738	0.0588	0.0308	0.0239	0.0192	0.0158	0.0145	0.0139
0.30	0.2338	0.7227	0.1099	0.0766	0.1111	0.1759	0.1738	0.0600	0.0320	0.0252	0.0204	0.0172	0.0159	0.0153
0.35	0.2269	0.7167	0.1116	0.0786	0.1126	0.1766	0.1745	0.0617	0.0335	0.0266	0.0219	0.0185	0.0170	0.0165
0.40	0.2288	0.7121	0.1142	0.0817	0.1151	0.1782	0.1762	0.0644	0.0361	0.0292	0.0244	0.0208	0.0194	0.0187
0.45	0.2221	0.7023	0.1121	0.0806	0.1143	0.1770	0.1750	0.0650	0.0370	0.0302	0.0255	0.0220	0.0205	0.0199
0.50	0.2257	0.6925	0.1120	0.0813	0.1149	0.1766	0.1748	0.0662	0.0383	0.0317	0.0268	0.0232	0.0218	0.0211
0.55	0.2165	0.6850	0.1135	0.0832	0.1160	0.1768	0.1752	0.0677	0.0399	0.0332	0.0285	0.0248	0.0234	0.0227
$\varepsilon_L{}^a$	12.0224	38.5775	5.4513	3.5278	5.3140	8.7199	8.5692	2.6253	1.2745	0.9130	0.6766	0.5220	0.4610	0.4438

[a] Molar absorptivities calculated from A_L/C_L in mM^{-1}cm^{-1}.

Table 3.4 Selected UV-VIS spectrophotometric titration data of ligand **:**Eu(III) system with metal to ligand ratio varied from 1 to 11, $C_{initial}$ of ligand and Eu(III) are 2.0×10^{-5} and 1.2×10^{-3} M, $V_{initial}$ is 3.00 cm^3.

Volume (cm^3)	Wavelength (nm)											
	220	230	240	250	260	270	280	290	300	310	320	330
0.05	0.2222	0.7391	0.1042	0.0562	0.0849	0.1510	0.1587	0.0587	0.0416	0.0398	0.0333	0.0227
0.10	0.2401	0.7290	0.1055	0.0589	0.0877	0.1531	0.1618	0.0630	0.0443	0.0423	0.0357	0.0250
0.15	0.2328	0.7070	0.0974	0.0541	0.0836	0.1490	0.1599	0.0630	0.0413	0.0396	0.0331	0.0226
0.20	0.2241	0.6999	0.0994	0.0564	0.0856	0.1504	0.1622	0.0662	0.0430	0.0412	0.0348	0.0244
0.25	0.2217	0.6899	0.0974	0.0544	0.0823	0.1457	0.1575	0.0625	0.0387	0.0370	0.0305	0.0203
0.30	0.2177	0.6846	0.0989	0.0555	0.0826	0.1450	0.1565	0.0628	0.0388	0.0374	0.0310	0.0211
0.35	0.2188	0.6800	0.0996	0.0561	0.0821	0.1436	0.1551	0.0618	0.0378	0.0363	0.0299	0.0198
0.40	0.2248	0.6763	0.1020	0.0581	0.0829	0.1434	0.1548	0.0619	0.0379	0.0366	0.0303	0.0203
0.45	0.2259	0.6733	0.1040	0.0594	0.0831	0.1424	0.1532	0.0606	0.0365	0.0352	0.0289	0.0190
0.50	0.2120	0.6685	0.1048	0.0598	0.0824	0.1404	0.1509	0.0598	0.0360	0.0347	0.0284	0.0186
0.55	0.2205	0.6660	0.1065	0.0609	0.0822	0.1396	0.1501	0.0595	0.0358	0.0347	0.0286	0.0190
ε_L [a]	11.1095	36.9571	5.2112	2.8097	4.2452	7.5497	7.9367	2.9356	2.0783	1.9895	1.6629	1.1349

[a] Molar absorptivities calculated from A_L/C_L in mM^{-1}cm^{-1}.

Table 3.5 Selected UV-VIS spectrophotometric titration data of ligand **:**Y(III) system with metal to ligand ratio varied from 1 to 11, $C_{initial}$ of ligand and Y(III) are 2.0 x 10^{-5} and 1.2x10^{-3} M, $V_{initial}$ is 3.00 cm^3.

Volume	Wavelength (nm)									
(cm^3)	210	220	230	240	250	260	270	280	290	300
0.05	0.2076	0.2155	0.7155	0.0913	0.0466	0.0753	0.1405	0.1467	0.0456	0.0283
0.10	0.2160	0.2180	0.7042	0.0901	0.0465	0.0755	0.1412	0.1489	0.0499	0.0316
0.15	0.2080	0.2075	0.6806	0.0820	0.0428	0.0735	0.1392	0.1498	0.0533	0.0312
0.20	0.1816	0.1985	0.6693	0.0795	0.0415	0.0722	0.1376	0.1493	0.0542	0.0308
0.25	0.1952	0.1926	0.6577	0.0757	0.0387	0.0693	0.1340	0.1462	0.0522	0.0287
0.30	0.2150	0.1992	0.6522	0.0768	0.0401	0.0707	0.1348	0.1472	0.0544	0.0309
0.35	0.2143	0.1936	0.6436	0.0742	0.0383	0.0683	0.1320	0.1448	0.0525	0.0293
0.40	0.1861	0.1902	0.6355	0.0729	0.0375	0.0671	0.1300	0.1426	0.0517	0.0289
0.45	0.1559	0.1805	0.6279	0.0710	0.0358	0.0652	0.1276	0.1401	0.0501	0.0275
0.50	0.2452	0.1953	0.6193	0.0696	0.0352	0.0642	0.1257	0.1381	0.0494	0.0273
0.55	0.1683	0.1851	0.6146	0.0684	0.0341	0.0629	0.1241	0.1366	0.0481	0.0264
ε_L[a]	10.3793	10.7758	35.7741	4.5666	2.3278	3.7645	7.0269	7.3346	2.2803	1.4147

[a] Molar absorptivities calculated from A_L/C_L in mM^{-1}cm^{-1}.

3.4 Quantum Chemical Calculations

3.4.1 Structure Optimization

The structure of calix[4]-cyclen-benzocrown-6, **L** and its protonated species were built by standard geometrical parameter of the HyperChem Release 7.0 for window.[39] Their structure were optimized by the semi-empirical AM1 method

3.4.2 *Ab initio* Calculations

The SCF energies of AM1 optimized structure were determined by *ab initio* Harthree-Fock with 6-31G basis set. The all possible species of calix[4]-cyclen-benzocrown-6, **L** and its protonated species were optimized and computed of their energies at the 6-31G level. The sequence of proton addition of protonation indicated by numbers are shown in Figure 3.1.

All calculations were performed on the Pentium II/350 IBM-PC300Gl with RAM 512 MB. The program Gaussian 94W[16] was used for energy calculations.
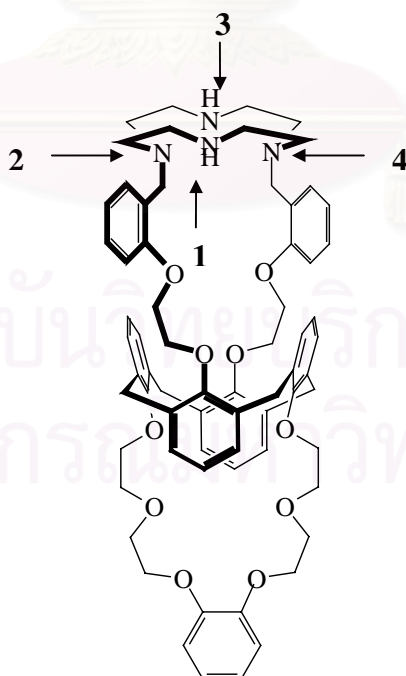
Figure 3.1 The sequence of proton addition of protonation on four cyclen nitrogen atoms of the ligand L.
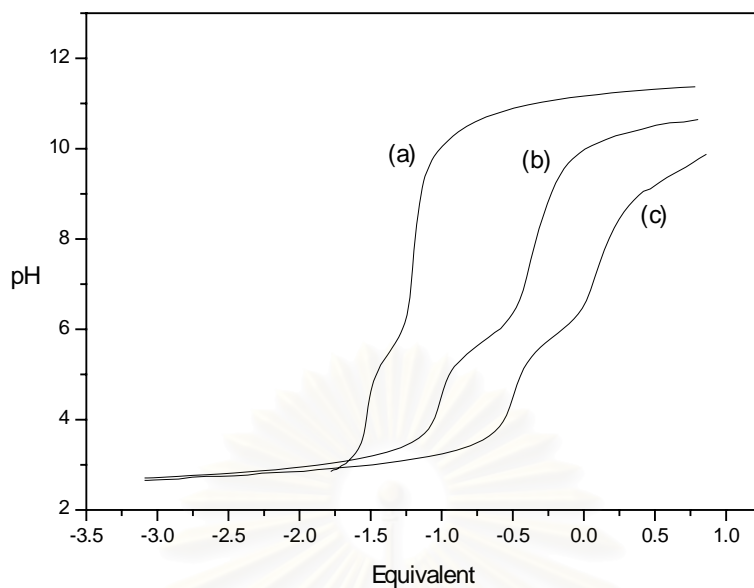
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Basicity Constant of Calix[4]-cyclen-benzocrown-6 (L)

Potentiometric titration curves of calix[4]-cyclen-benzocrown-6 (L) in 1×10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH at 25 °C, based on the various initial ratio of the ligand to proton are shown in Figure 4.1. At least 40 points of each titrations were used in computer refinements to obtain protonation constants which were calculated using the programe SUPERQUAD.[18] The protonation constants of calix[4]-cyclen-benzocrown-6 (L) expressed in terms of logarithm of its values in 1×10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH, at 25 °C are shown in Table 4.1.

Table 4.1 Logarithm of protonation constants of calix[4]-cyclen-benzo-crown-6 (L) in 1×10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH, at 25 °C.

Protonation						Log K
K_1 :	L	+	H^+	$\rightleftharpoons$	LH^+	10.91 ± 0.13
K_2 :	LH^+	+	H^+	$\rightleftharpoons$	LH_2^{2+}	10.30 ± 0.25
K_3 :	LH_2^{2+}	+	H^+	$\rightleftharpoons$	LH_3^{3+}	6.24 ± 0.26
K_4 :	LH_3^{3+}	+	H^+	$\rightleftharpoons$	LH_4^{4+}	2.55 ± 0.28

Distribution curves of various species of calix[4]-cyclen-benzo-crown-6 (L) in 1×10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH at 25 °C, $C_L = 9.1 \times 10^{-3}$ M are shown in Figure 4.2.

Figure 4.1 Potentiometric titration curves of calix[4]-cyclen-benzo-crown-6 in 1×10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH based on the initial concentration ratio of the ligand to proton (a) 1:1.32, (b) 1:2.42 and (c) 1:3.39; equivalent is defined as ratio of ($n_{OH^-} - n_{acid}$) to n_{ligand}.
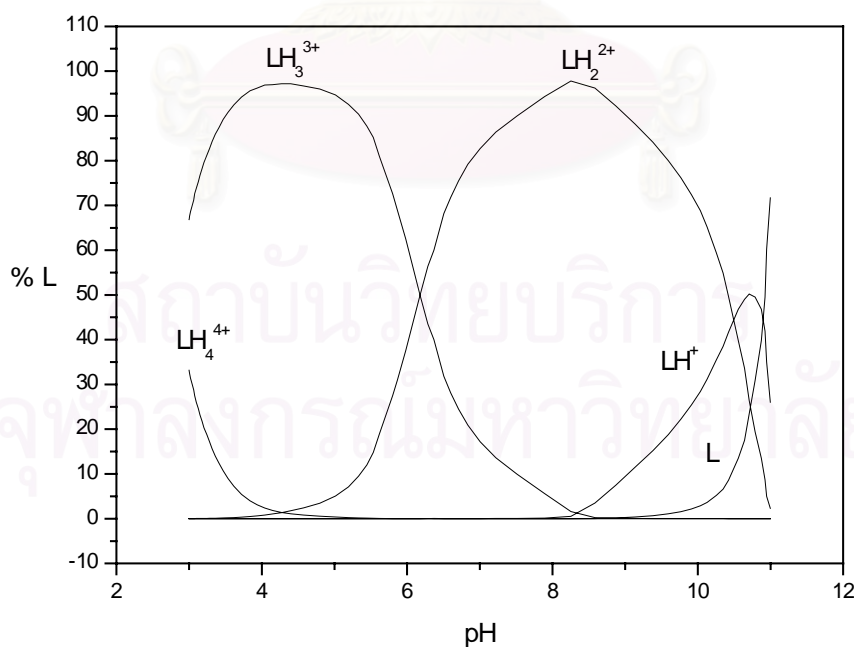
Figure 4.2 Distribution curves of calix[4]-cyclen-benzo-crown-6 in 1×10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH at 25 °C, $C_L = 9.1 \times 10^{-3}$ M

Figure 4.2, the species distribution curve of calix[4]-cyclen-benzo-crown-6 in 1 x 10^{-2} M Bu$_4$NCF$_3$SO$_3$ in 40% CH$_2$Cl$_2$/CH$_3$OH at 25 °C, shows that the LH$_4^{4+}$ species is steeply decrease from around 30% mole at pH 2.6 to less than 5% at pH higher than 4.0. Over 70% of the LH$_3^{3+}$ species exists within the pH range of 3.1 to 5.8.The LH$_2^{2+}$ species exists within the pH range of 4 to 11.The maximun percent of LH$_2^{2+}$ species appears at pH 8.3 (97%). The LH$^+$ species exists within the pH range of 8.3 to ~11.The maximun percent of LH$^+$ species appears at pH 10.6 (50%). The free ligand species, L exits at pH higher than ~9.5 and its highest population is steeply increased at higher pH. The present species of L in 1 x 10^{-2}M Bu$_4$NCF$_3$SO$_3$ in 40% CH$_2$Cl$_2$/CH$_3$OH depend on pH of solution is shown in Table 4.2.

Table 4.2 Existing species of calix[4]-cyclen-benzo-crown-6 in 1 x 10^{-2} M Bu$_4$NCF$_3$SO$_3$ in 40% CH$_2$Cl$_2$/CH$_3$OH at 25 °C, depending on the pH of solution.

Species	pH range
L	> ~9
LH$^+$	8.3 to ~11
LH$_2^{2+}$	4 to ~11
LH$_3^{3+}$	~3 to ~8.3
LH$_4^{4+}$	< ~4.5

**4.2 Complexation Constant by UV-VIS spectrophotometry**

Uv spectrophotometric data obtained from uv titration of ligand **L**/Cu(II) (Table 3.2), ligand **L**/Zn(II) (Table 3.3), ligand **L**/Eu(III) (Table 3.4) and ligand **L**/Y(III) systems (Table 3.5) are shown in Figures 4.3 and 4.4, 4.5 and 4.6, 4.7 and 4.8, respectively.
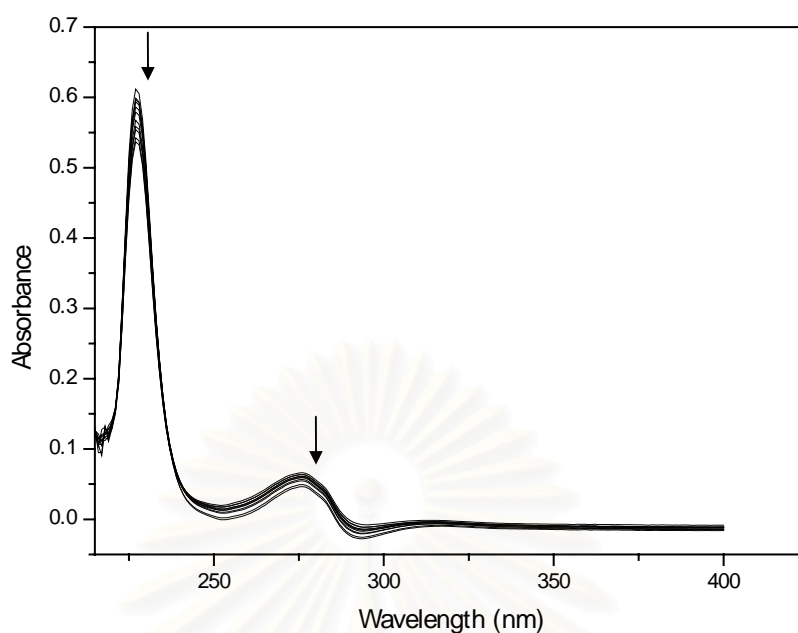
Figure 4.3 UV spectra obtained from uv spectrophotometric titration for ligand **L**/Cu(II) system which Cu(II): ligand **L** ratio varied from 0.1 to 1. (downward and upward symbols correspond to decreased and increased absorbances, respectively.)
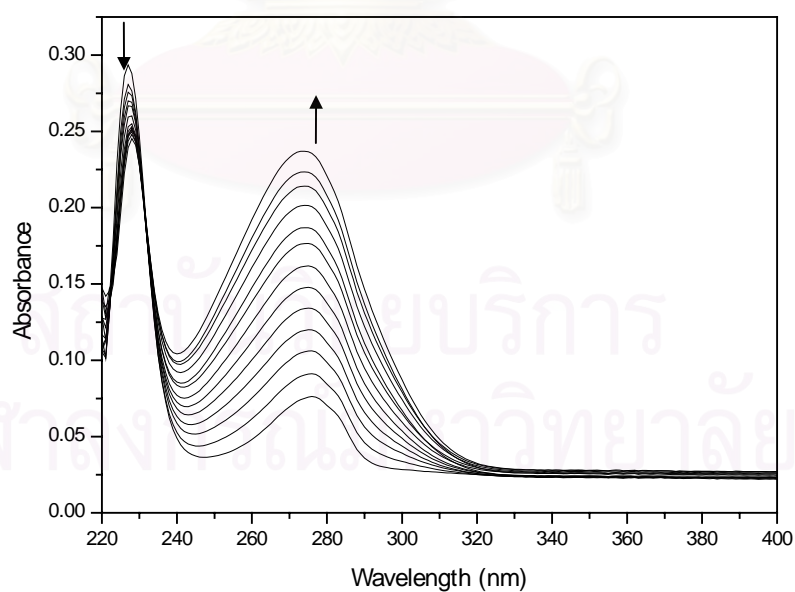
Figure 4.4 UV spectra obtained from uv spectrophotometric titration for ligand **L**/Cu(II) system which Cu(II): ligand **L** ratio varied from 1 to 11. (downward and upward symbols correspond to decreased and increased absorbances, respectively.)
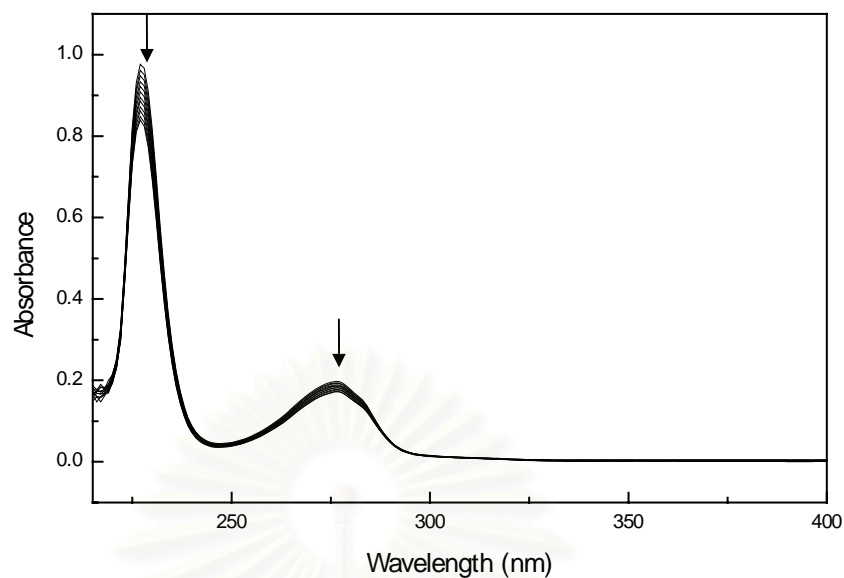
Figure 4.5 UV spectra obtained from uv spectrophotometric titration for ligand **L**/Zn(II) system which Zn(II): ligand **L** ratio varied from 1 to 11. (downward and upward symbols correspond to decreased and increased absorbances, respectively.)
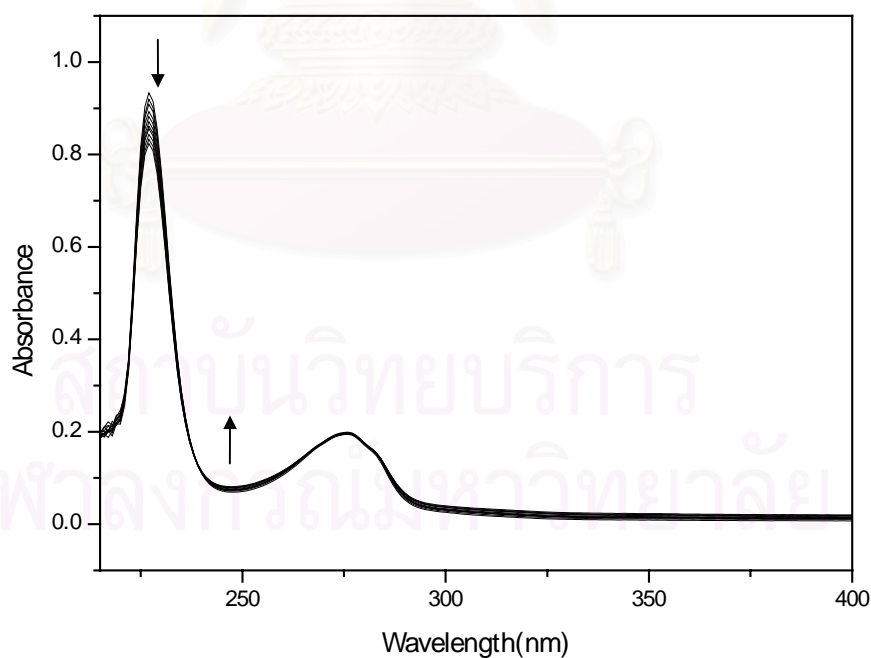

Figure 4.6 UV spectra obtained from uv spectrophotometric titration for ligand **L**/Zn(II) system which Zn(II): ligand **L** ratio varied from 10 to 110. (downward and upward symbols correspond to decreased and increased absorbances, respectively.)

Figure 4.7 UV spectra obtained from uv spectrophotometric titration for ligand **L**/Eu(III) system which Eu(III): ligand **L** ratio varied from 1 to 11. (downward and upward symbols correspond to decreased and increased absorbances, respectively.)
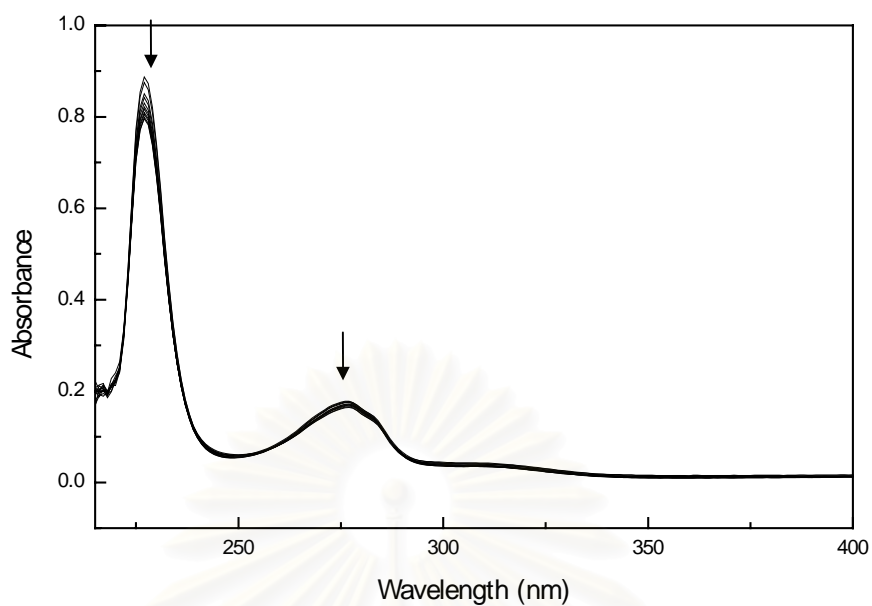

Figure 4.8 UV spectra obtained from uv spectrophotometric titration for ligand **L**/Y(III) system which Y(III): ligand **L** ratio varied from 1 to 11. (downward and upward symbols correspond to decreased and increased absorbances, respectively.)
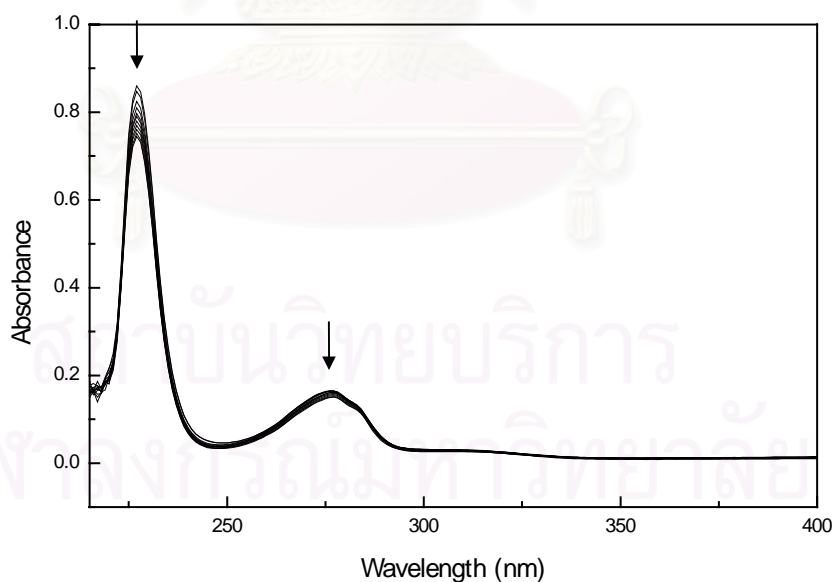
Figure 4.3 and 4.4 are the UV spectra of the titrations for ligand L/Cu(II) system which Cu(II) to ligand L ratio varied from 0.1 to 1 and 1 to 11, respectively. The selected spectral data from UV spectrophotometric titration of Figure 4.4 as shown in Table 3.2(b) were used in the evalution of stability constants of L/Cu(II) complex system by SIRKO program. The UV spectrophotometric titration data of Figure 4.3 gives the poor absorbance in compare with the dilution effect according to the very low concentration of Cu(II) titrant. On the other hand, at the high concentration of Cu(II) titrant, the UV spectrophotometric titration data of Figure 4.4 can be used to evaluate the stability of Cu (II)/L complex system because the spectral absorbances of the complex are increased while the spectral absorbance of ligand L as reactance are decreased as indicated by the existing of isobestic point. Figures 4.5 and 4.6 are the UV spectra of the titrations for ligand L/Zn(II) system which Zn(II) to ligand L ratio varied from 1 to 11 and 10 to 110, respectively. The selected spectral data from UV spectrophotometric titration of Figure 4.6 as shown in Table 3.3(b) were used in the evalution of stability constants of L/Zn(II) complex system by SIRKO program. The UV spectrophotometric titration data of Figure 4.5 gives the poor absorbance in compare with the dilution effect according to the very low concentration of Zn(II) titrant. At the high concentration of Zn(II) titrant, the UV spectrophotometric titration data of Figure 4.6 can be used to evaluate the stability of Zn (II)/L complex system because the spectral absorbances of the complex are increased while the spectral absorbance of ligand as reactance are decreased as indicated by the existing of isobestic point. Figures 4.7 and 4.8 show that the UV spectra obtained from the UV spectrophotometric titrations for ligand L/Eu(III) and L/Y(III) systems give poor absorbances of spectra. Due to their poor spectral absorptivies, complexation between ligand L and Eu(III) and Y(III) cations were not formed .

The stability constants of ligand L complexing with Cu(II) and Zn(II) in 1×10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH at 25 °C, in the form of log β are shown in Table 4.3

Table 4.3 Stability constants (Log β) of calix[4]-cyclen-benzo-crown-6 complex with Cu (II) and Zn(II) in 1 x 10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH, at 25 °C.

ligand L/M(II) Complex	Log β
Cu(II)	4.37$\pm$0.005
Zn(II)	3.45$\pm$0.005

4.3 Quantum Chemical Calculations

4.3.1 Structure optimization

Structure of calix[4]-cyclen-benzo-crown-6 and its zinc complex obtained from the AM1-optimizations are shown in Figure 4.10

(a)   (b)
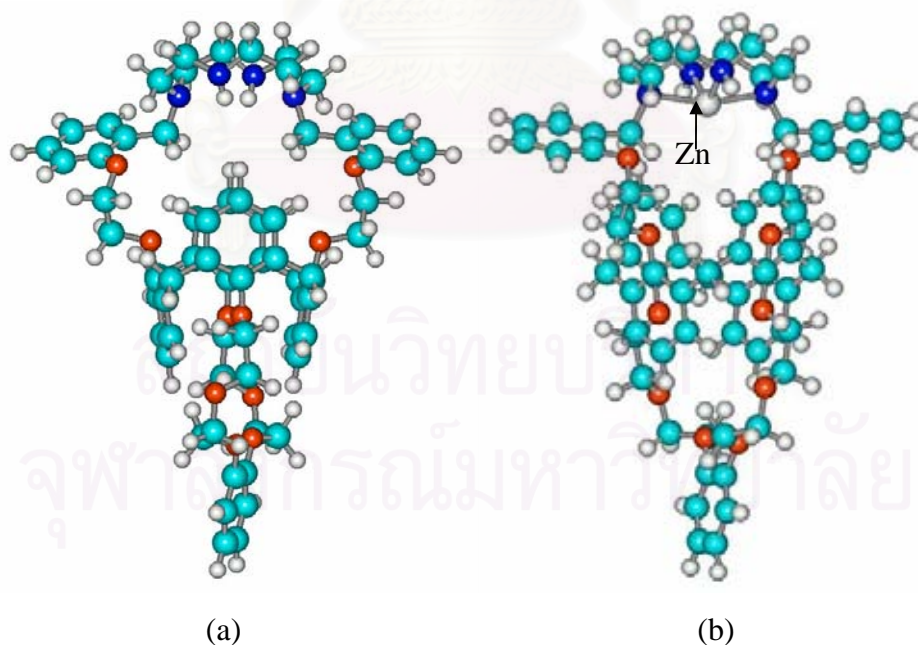
Figure 4.9 The optimized strucure of (a) calix[4]-cyclen-benzo-crown-6 and (b) its zinc complex obtained by semi-empirical AM1.

4.3.2 Energy Calculations.

The total energies of the AM1 optimized structures of calix[4]-cyclen-benzocrown-6, **L** and its complex with Zn(II) were calculated by *ab initio* HF method with 6-31G basis set are shown in Table 4.4. The possible pre-organized structure of the protonation of calix[4]-cyclen-benzo-crown-6, **L** were calculated by *ab initio* HF method with 6-31G basis set are shown in Table 4.5.

Table 4.4 Total energies (E) of AM1-optimized structures of the calix[4]-cyclen-benzo-crown-6, its protonated species and its complex with Zn(II) calculated by *ab initio* HF method with 6-31G basis set.

Species [a]	E (hartrees)
L	-3585.0728965
LH^1	-3585.5343653
LH^1H^2 [b]	-3585.5352576
LH^1H^3	-3585.8396573
LH^2	-3585.5352576
LH^2H^4	-3585.8618742
$LH^1H^2H^3$ [c]	-3586.0228085
$LH^1H^2H^4$ [d]	-3586.0607310
$LH^1H^2H^3H^4$ [e]	-3586.1036090
Zn^{2+}	-1776.6120740
$(ZnL)^{2+}$	-5362.2750858

[a] Species of $LH^1H^2H^3H^4$ is defined as protonation sequence of the first, second, third and fourth position (shown in Figure 3.1).

[b] $E_{LH^1H^2}$ and $E_{LH^2H^1}$ are identical.

[c] $E_{LH^1H^2H^3}$ and $E_{LH^1H^3H^2}$ are identical.

[d] $E_{LH^1H^2H^4}$ and $E_{LH^2H^4H^1}$ are identical.

[e] $E_{LH^1H^2H^3H^4}$, $E_{LH^1H^3H^2H^4}$, $E_{LH^1H^2H^4H^3}$, $E_{LH^2H^1H^3H^4}$, $E_{LH^2H^1H^4H^3}$ and $E_{LH^2H^4H^1H^3}$ are identical.

Table 4.5 Total energies of all possible pre-organized structures of the protonation of calix[4]-cyclen-benzo-crown-6, **L** calculated by *ab initio* HF method with 6-31G basis set.

Species	E (hartrees)
$L(H^1)$	-3585.0585883
$LH^1(H^2)$	-3585.4991223
$LH^1(H^3)$	-3585.5026857
$L(H^2)$	-3585.0704882
$LH^2(H^4)$	-3585.5046255
$LH^1H^2(H^3)$	-3585.8112493
$LH^1H^2(H^4)$	-3585.8201605
$LH^1H^2H^3(H^4)$	-3585.9482545
$LH^1H^2H^4(H^3)$	-3585.9818593
$LH^2H^4(H^1)$	-3585.8110360
$LH^2(H^1)$	-3585.4792418

H atom in parathesis is a removed atom. Most right H atom is the last binding proton.

The protonation process of possible pathways of the conformation of calix[4]-cyclen-benzo-crown-6, **L** are shown in Table 4.6.

Table 4.6 The protonation process of possible pathways of the conformation of calix[4]-cyclen-benzo-crown-6, **L**.

1st pathway :	$L \xrightarrow{\Delta E_1^{(1)}} LH^1 \xrightarrow{\Delta E_2^{(1)}} LH^1H^2 \xrightarrow{\Delta E_3^{(1)}} LH^1H^2H^3 \xrightarrow{\Delta E_4^{(1)}} LH^1H^2H^3H^4$
2nd pathway :	$L \xrightarrow{\Delta E_1^{(2)}} LH^1 \xrightarrow{\Delta E_2^{(2)}} LH^1H^2 \xrightarrow{\Delta E_3^{(2)}} LH^1H^2H^4 \xrightarrow{\Delta E_4^{(2)}} LH^1H^2H^3H^4$
3rd pathway :	$L \xrightarrow{\Delta E_1^{(3)}} LH^1 \xrightarrow{\Delta E_2^{(3)}} LH^1H^3 \xrightarrow{\Delta E_3^{(3)}} LH^1H^2H^3 \xrightarrow{\Delta E_4^{(3)}} LH^1H^2H^3H^4$
4th pathway :	$L \xrightarrow{\Delta E_1^{(4)}} LH^2 \xrightarrow{\Delta E_2^{(4)}} LH^1H^2 \xrightarrow{\Delta E_3^{(4)}} LH^1H^2H^3 \xrightarrow{\Delta E_4^{(4)}} LH^1H^2H^3H^4$
5th pathway :	$L \xrightarrow{\Delta E_1^{(5)}} LH^2 \xrightarrow{\Delta E_2^{(5)}} LH^1H^2 \xrightarrow{\Delta E_3^{(5)}} LH^1H^2H^4 \xrightarrow{\Delta E_4^{(5)}} LH^1H^2H^3H^4$
6th pathway :	$L \xrightarrow{\Delta E_1^{(6)}} LH^2 \xrightarrow{\Delta E_2^{(6)}} LH^2H^4 \xrightarrow{\Delta E_3^{(6)}} LH^1H^2H^4 \xrightarrow{\Delta E_4^{(6)}} LH^1H^2H^3H^4$

The protonation energies, ΔE of conformation of calix[4]-cyclen-benzo-crown-6, **L** and stabilization energy, $\Delta E_{complex}$ calculated by *ab initio* HF method with 6-31G basis set are shown in Table 4.7.
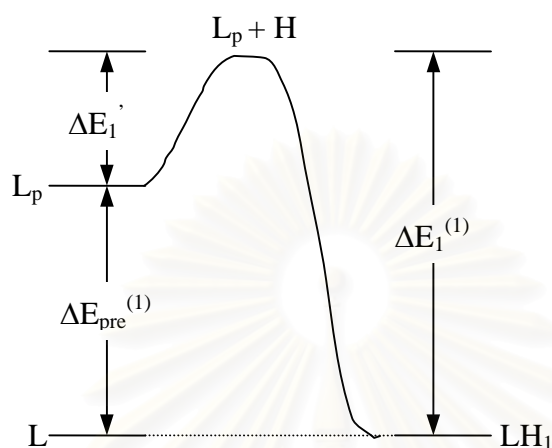
Table 4.7 The protonation energies of calix[4]-cyclen-benzo-crown-6, **L**, and stabilization energies of its zinc complex calculated by *ab initio* HF method with 6-31G basis set.

Protonation	ΔE (kcal/mol) (without cp[a])
$\Delta E_1^{(1)} = \Delta E_1^{(2)} = \Delta E_1^{(3)}$: L $\longrightarrow$ LH^1	-289.6
$\Delta E_2^{(1)} = \Delta E_2^{(2)}$: LH^1 $\longrightarrow$ LH^{1}H^2	-200.0
$\Delta E_3^{(1)} = \Delta E_3^{(4)}$: LH^{1}H^2 $\longrightarrow$ LH^{1}H^{2}H^3	-106.6
$\Delta E_4^{(1)} = \Delta E_4^{(3)} = \Delta E_4^{(4)}$: LH^{1}H^{2}H^3 $\longrightarrow$ LH^{1}H^{2}H^{3}H^4	-50.7
$\Delta E_3^{(2)} = \Delta E_3^{(5)}$: LH^{1}H^2 $\longrightarrow$ LH^{1}H^{2}H^4	-130.4
$\Delta E_4^{(2)} = \Delta_4^{(5)} = \Delta E_4^{(6)}$: LH^{1}H^{2}H^4 $\longrightarrow$ LH^{1}H^{2}H^{3}H^4	-26.9
$\Delta E_2^{(3)}$: LH^1 $\longrightarrow$ LH^{1}H^3	-204.1
$\Delta E_3^{(3)}$: LH^{1}H^3 $\longrightarrow$ LH^{1}H^{2}H^3	-114.9
$\Delta E_1^{(4)} = \Delta E_1^{(5)} = \Delta E_1^{(6)}$: L $\longrightarrow$ LH^2	-290.1
$\Delta E_2^{(4)} = \Delta E_2^{(5)}$: LH^2 $\longrightarrow$ LH^{1}H^2	-199.4
$\Delta E_2^{(6)}$: LH^2 $\longrightarrow$ LH^{2}H^4	-205.0
$\Delta E_3^{(6)}$: LH^{2}H^4 $\longrightarrow$ LH^{1}H^{2}H^4	-124.9
$\Delta E_{complex}$: L + Zn^{2+} $\longrightarrow$ (ZnL)$^{2+}$	-370.3

[a] stands for counterpoise correction.

Tables 4.6 and 4.7 indicate that the most stable pathway of protonation process is a sixth pathway.

Pre-organization energies of calix[4]-cyclen-benzocrown-6, **L** and all possible structures of its protonated species are shown in Figure 4.10 and 4.11, respectively.

Scheme 4.1 Pre-organization and protonation energies diagram of calix[4]-cyclen-benzocrown-6, **L**

Protonation energy defined as summation of

$$\Delta E_1^{(1)} = \Delta E_{pre\text{-}org}^{(1)} + \Delta E_1^{'} \tag{4.1}$$

Where $\Delta E_{pre}^{(1)}$, $\Delta E_1^{'}$ and $\Delta E_1^{(1)}$ are pre-organization, binding and protonation energies, respectively.

1 :

$$L \xrightarrow{\Delta E_{pre}^{\ 1} = \ 9.0} L_p \xrightarrow{\Delta E_1' = -222.1} LH^1$$

$$\Delta E_1^{(1)} = -289.6$$

2 :

$$LH^1 \xrightarrow{\Delta E_{pre}^{\ 2} = \ 22.1} LH^1_p \xrightarrow{\Delta E_2' = -222.1} LH^1H^2$$

$$\Delta E_2^{(1)} = -200.0$$

3 :

$$LH^1H^2 \xrightarrow{\Delta E_{pre}^{\ 3} = \ 26.2} LH^1H^2_p \xrightarrow{\Delta E_3' = -132.8} LH^1H^2H^3$$

$$\Delta E_3^{(1)} = -106.6$$

4 :

$$LH^1H^2H^3 \xrightarrow{\Delta E_{pre}^{\ 4} = \ 46.8} LH^1H^2H^3_p \xrightarrow{\Delta E_4' = -97.5} LH^1H^2H^3H^4$$

$$\Delta E_4^{(3)} = -50.7$$

5 :

$$LH^1H^2 \xrightarrow{\Delta E_{pre}^{\ 5} = \ 20.6} LH^1H^2_p \xrightarrow{\Delta E_5' = -151.1} LH^1H^2H^4$$

$$\Delta E_3^{(2)} = -130.4$$

6 :

$$LH^1H^2H^4 \xrightarrow{\Delta E_{pre}^{\ 6} = \ 49.5} LH^1H^2H^4_p \xrightarrow{\Delta E_6' = -76.4} LH^1H^2H^3H^4$$

$$\Delta E_4^{(5)} = -26.9$$

7 :

$$LH^1H^3 \xrightarrow{\Delta E_{pre}^{\ 7} = \ 29.0} LH^1H^3_p \xrightarrow{\Delta E_7' = -143.91} LH^1H^3H^2$$

$$\Delta E_3^{(3)} = -114.9$$

8 :

$$LH^1H^3H^2 \xrightarrow{\Delta E_{pre}^{\ 8} = \ 46.8} LH^1H^3H^2_p \xrightarrow{\Delta E_8' = -97.5} LH^1H^3H^2H^4$$

$$\Delta E_4^{(3)} = -114.9$$

9 : $\quad$ L $\xrightarrow{\quad \Delta E_{pre}^{\ 9} = 1.5 \quad}$ L_p $\xrightarrow{\quad \Delta E_9{}' = -291.1 \quad}$ LH^2

$$\Delta E_1^{\ (4)} = -290.1$$

10 : $\quad$ $LH^2 \xrightarrow{\quad \Delta E_{pre}^{\ 10} = 35.2 \quad}$ LH^2_p $\xrightarrow{\quad \Delta E_{10}{}' = -234.5 \quad}$ LH^2H^1

$$\Delta E_2^{\ (6)} = -199.4$$

11 : $\quad$ $LH^2 \xrightarrow{\quad \Delta E_{pre}^{\ 11} = 19.2 \quad}$ LH^2_p $\xrightarrow{\quad \Delta E_{11}{}' = -224.2 \quad}$ LH^2H^4

$$\Delta E_2^{\ (6)} = -205.0$$

12 : $\quad$ $LH^2H^4 \xrightarrow{\quad \Delta E_{pre}^{\ 12} = 31.9 \quad}$ $LH^2\,H^4_p$ $\xrightarrow{\quad \Delta E_{12}{}' = -156.7 \quad}$ $LH^2H^4H^1$

$$\Delta E_3^{\ (6)} = -124.9$$

Figure 4.11 The pre-organization energies and pre-organized protonation of calix[4]-cyclen-benzo-crown-6, **L**.

The stabilization energies, ΔE of all possible structures of protonated calix[4]-cyclen-benzocrown-6, **L** calculated by *ab initio* HF method with 6-31G basis set are shown in Table 4.8.

Table 4.8 The protonation energies of the protonated calix[4]-cyclen-benzo-crown-6, **L** calculated by *ab initio* HF method with 6-31G basis set.

Path ways (kcal/mol)	ΔE_{pre} (kcal/mol) (without cp[a])	$\Delta E'$ (kcal/mol) (without cp[a])	ΔE (kcal/mol)
1	$\Delta E^1 = 9.0$	$\Delta E_1' = -298.6$	$\Delta E_1^{(1)} = -289.6$
2	$\Delta E^2 = 22.1$	$\Delta E_2' = -222.1$	$\Delta E_2^{(1)} = -200.0$
3	$\Delta E^3 = 26.2$	$\Delta E_3' = -132.8$	$\Delta E_3^{(1)} = -106.6$
4	$\Delta E^4 = 46.8$	$\Delta E_4' = -97.5$	$\Delta E_4^{(4)} = -50.7$
5	$\Delta E^5 = 20.6$	$\Delta E_5' = -151.1$	$\Delta E_3^{(2)} = -130.4$
6	$\Delta E^6 = 49.5$	$\Delta E_6' = -76.4$	$\Delta E_4^{(5)} = -26.9$
7	$\Delta E^7 = 29.0$	$\Delta E_7' = -143.9$	$\Delta E_3^{(3)} = -114.9$
8	$\Delta E^8 = 46.8$	$\Delta E_8' = -97.5$	$\Delta E_4^{(3)} = -50.7$
9	$\Delta E^9 = 1.5$	$\Delta E_9' = -291.6$	$\Delta E_1^{(4)} = -290.1$
10	$\Delta E^{10} = 35.2$	$\Delta E_{10}' = -234.5$	$\Delta E_2^{(6)} = -199.4$
11	$\Delta E^{11} = 19.2$	$\Delta E_{11}' = -224.2$	$\Delta E_2^{(6)} = -205.0$
12	$\Delta E^{12} = 31.9$	$\Delta E_{12}' = -156.7$	$\Delta E_3^{(6)} = -124.9$

[a] stands for counterpoise correction.

The *ab initio* energies, E with 6-31G basis set including the counterpoise procedure of corresponding subsystem A, B and protonation system (AB), and the stabilization energy, ΔE of the protonated conformations of calix[4]-cyclen-benzo-crown-6, **L** species A, B and AB denote subsystem of reactance A and B (proton), and system of protonation, respectively are shown in Table 4.9.

Table 4.9 The *ab initio* energies, E with 6-31G basis set including the counterpoise procedure of the corresponding subsystem A, B and protonation system (AB), and stabilization energy, ΔE of the protonated of calix[4]-cyclen-benzo-crown-6, **L** species A, B and AB denote subsystem of reactance A and B (proton), and system of protonation, respectively.

Protonated species	E_{AB} (hartree)	E_A (hartree)	ΔE (kcal/mol)
LH^1	-3585.5343653	-3585.0641367	-295.07
LH^1H^2	-3585.8529891	-3585.5102138	-215.11
LH^1H^3	-3585.8396573	-3585.5070552	-208.71
LH^2	-3585.5352576	-3585.0769354	-287.60
LH^2H^4	-3585.8618742	-3585.5136737	-218.50
$LH^1H^2H^3$	-3586.0228085	-3585.8133478	-131.44
$LH^1H^2H^4$	-3586.0607310	-3585.8162371	-153.42
$LH^1H^2H^3H^4$	-3586.1036090	-3585.9574746	-91.70
$LH^1H^3H^2$	-3586.0228085	-3585.7915415	-145.12
LH^2H^1	-3585.8529891	-3585.4745811	-237.47
$LH^2H^4H^1$	-3586.0607310	-3585.8122819	-155.90
$LH^1H^2H^4H^3$	-3586.1036090	-3585.9883177	-72.35

$E_B = E_{H^+} = 0$; E_A and E_{AB} of $LH^1H^2H^3H^4$ is identical to E_A and E_{AB} of $LH^1H^3H^2H^4$

Table 4.8 and 4.9 show that the energy of HF/6-31G with counterpoise correction better than HF/6-31G without counterpoise correction .

CHAPTER V

CONCLUSION

The calix[4]-cyclen-benzo-crown-6, **L** was synthesized by the produce is reference 35. Basicity of the ligand L have been studied in terms of protonation constants by potentiometric titrations. The protonation constants of ligand L in 1 x 10^{-2} M $Bu_4NCF_3SO_3$ in 40 %CH_2Cl_2/CH_3OH, at 25 °C are log $K_1 = 10.91\pm0.13$, log $K_2 = 10.30\pm0.25$, log $K_3 = 6.24\pm0.26$ and log $K_4 = 2.55\pm0.28$, respectively. Dominant species of LH_4^{4+}, LH_3^{3+}, LH_2^{2+}, LH^+ and L in 1 x 10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH depending on the pH of solution are existing in pH range of <~ 4.5, ~3 to ~8.3, a to ~11, 8.3 to 11 and greater than pH~9, respectively.

Stability constants for the calix[4]-cyclen-benzo-crown-6, **L** complexes with Cu (II) and Zn(II) ions in 1 x 10^{-2} M $Bu_4NCF_3SO_3$ in 40% CH_2Cl_2/CH_3OH, at 25 °C were determined by UV-VIS spectrometric titrations. The complexation constants in terms of log β of complexes between ligand L and Cu(II) and Zn(II) are 4.37 ± 0.005 and 3.45 ± 0.005, respectively. The complexation constant, log β of complexes between ligand L and Eu(II) and Y(III) are not detectable. The low selectivity of the ligand L for Cu(II) in comparison with Zn(II) is concluded.

Optimized structures of calix[4]-cyclen-benzo-crown-6, **L** and its related species were obtained by semi-empirical AM1 method. Stabilization energies for protonations of ligand L and complexation energies of its Zn(II) complex computed by HF/6-31G method are as follow :

Reaction	Stabilization energies (kcal/mol)
first protonation	-290.1
scond protonation	-205.0
third protonation	-124.9
fourth protonation	-26.9
complexation of $(ZnL)^{2+}$	-370.3

Suggestion for Future Works

Future works should be focused on :

1. Complexation studies of this ligand L with other metal ions such as Co^{2+}, Ni^{2+},Pb^{2+} and Pd^{2+} and with alkali ions such as Na^+, Li^+ and K^+.

2. Complexation studies of this ligand L with mixed ions by spectrometric titrations.

3. Structure of L and its related species should be optimized by *ab initio* method using STO-3G and the better basis sets instead of semi-empirical AM1 method.

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