จุฬาลงกรณ์มหาวิทยาลัย
ทุนวิจัย
กองทุนรัชดาภิเษกสมโภช

รายงานผลการวิจัย
เรื่อง

การตรวจสอบความเป็นกรดและเบสของอนุพันธ์ชนิดใหม่ของสารประกอบซาเลนและความเสถียรของสารประกอบเชิงซ้อนกับโลหะแคตไอออน

โดย

วิทยา เรืองพรวิสุทธิ์

กรกฎาคม ๒๕๔๕

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CU
วท 15
011446

Chulalongkorn University

Rachadapiseksompoj Research Fund

Research Report

Acidity and Basicity Investigation for Novel Derivative of Salen and Stabilities of Their Complexes with Metal Cations

by

Vithaya Ruangpornvisuti

July 2002

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

จุฬาลงกรณ์มหาวิทยาลัย

ทุนวิจัย
กองทุนรัชดาภิเษกสมโภช

รายงานผลการวิจัย

การตรวจสอบความเป็นกรดและเบสของอนุพันธ์ชนิดใหม่ของสารประกอบซาเลน และ ความเสถียรของสารประกอบเชิงซ้อนกับโลหะแคตไอออน

โดย

วิทยา เรืองพรวิสุทธิ์

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

กรกฎาคม 2545

ACKNOWLEDGEMENT

The work was supported by the Rachadapiseksompoj Research Fund, Research Affairs, Chulalongkorn University. The Supramolecular Chemistry Laboratory Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University is acknowledged as the main research laboratory. We thank Mr. Viwat Vchirawongkwin for his help on computing.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

เลขหมู่ eป
กท 15
เลขทะเบียน 011446
วัน,เดือน,ปี 19 กพ. 46

ชื่อโครงการ การตรวจสอบความเป็นกรดและเบส ของอนุพันธ์ชนิดใหม่ของสาร-ประกอบซาเลน และ ความเสถียรของสารประกอบเชิงซ้อนกับโลหะแคตไอออน

ชื่อผู้วิจัย วิทยา เรืองพรวิสุทธิ์
เดือนและปีที่ทำวิจัยเสร็จ กรกฎาคม 2545

บทคัดย่อ

การสังเคราะห์สารประกอบซาเลน 4 และ การหาค่าคงที่โปรโตเนชันโดยวิธีโพเทนชิโอเมทริกไทเทรชันโดยมีค่าในเทอมลอการิทึมเป็น log K_1=10.06, log K_2=7.96, log K_3=7.12, log K_4=3.28 และ log K_1=10.48, log K_2=7.99, log K_3=4.71, log K_4=2.77 ในสารละลาย 0.1 และ 0.5 M KNO_3 ณ 25 °C ตามลำดับ ค่าคงที่ความเสถียรของสารประกอบเชิงซ้อนระหว่างสารประกอบ 4 กับโลหะไอออน Ni(II), Cu(II) และ Zn(II) ในสารละลาย 0.01 M $Bu_4NCF_3SO_3$ ในเมทานอล โดยวิธียูวีวิสสเปกโตรเมตริกไทเทรชัน พบว่ามีค่า log β11 เท่ากับ 3.80, 4.28 และ 4.37 ตามลำดับ

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Project Title **Acidity and Basicity Investigation for Novel Derivative of Salen and Stabilities of Their Complexes with Metal Cations**

Name of investigator Vithaya Ruangpornvisuti

Year July 2002

Abstract

Salen derivative, **4** was synthesized and studied for determination of its protonation constants by potentiometric titration. The protonation constants at 25 °C in 0.1 and 0.5 M KNO_3 are log K_1=10.06, log K_2=7.96, log K_3=7.12, log K_4=3.28 and log K_1=10.48, log K_2=7.99, log K_3=4.71, log K_4=2.77, respectively. Complexation for the **4** complexes with Ni(II), Cu(II) and Zn(II) in 0.01 M $Bu_4NCF_3SO_3$ in MeOH were determined by UV-VIS spectrometric titration. The Stability constants, in terms of log β_{11}, of the **4** complexes with Ni(II), Cu(II) and Zn(II) are 3.80, 4.28 and 4.37, respectively.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS

Page

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Page

LIST OF FIGURES

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER I

INTRODUCTION

1.1 Review of Salen

Complexes of salen compounds with transition metal ions have been widely synthesized and studied. Mn(salen) complex [1-3] has been used as catalyst for oxidation reaction, known as Jacobsen's catalyst [4]. Salen complex with Ni(II) [5, 6] has been used in kinetic study of ligand transfer reaction and separation of DNA. Salen complex with Cu(II) [7 - 10] has been used for investigation of oxygenation reaction. Fe(salen) complex [11] has applied to be catalyst for oxidation polymerization.

Synthesis of new salen compounds and their acidity, basicity and stability of their complexes with transition metals should be interesting ways to investigate their chemical properties and make new catalysts for using in many reactions. The basic compound of salen shown in Figure 1.1 is a most simple structure with two hydroxide and two shift bases.

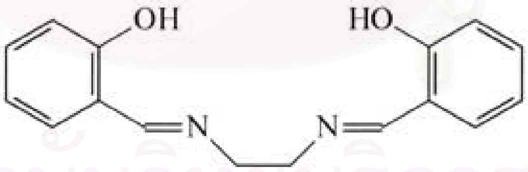


Figure 1.1 A basic unit of salen compound

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

The basic salen forming to cobalt has been used as well known catalyst called "Saldomine". The full name of saldomine is *N,N'*-Bis(salicylidene)-ethylenediaminocobalt(II). The common derivatives of salen, alkylated by R_1 and R_2 at para positions of both site of aromatic rings is shown in Figure 1.2. Polyoxo derivatives of salen as show in Figure 1.3, are the compounds of investigation in this research.

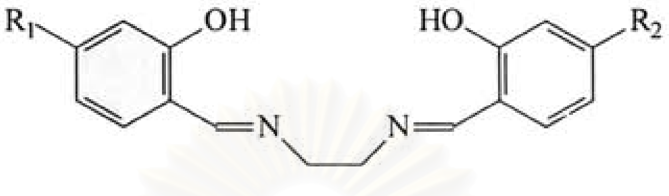
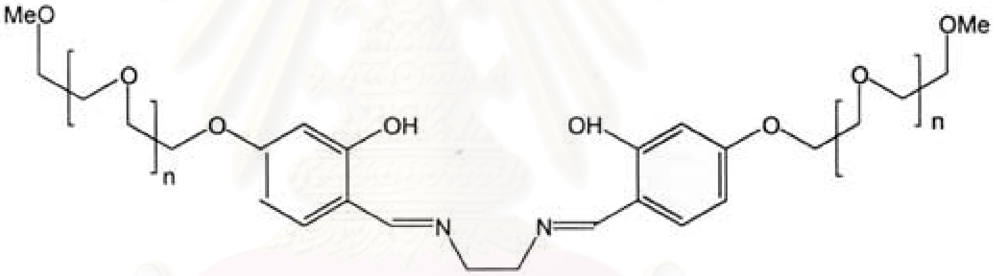


Figure 1.2 General structural fomula of salen derivative



1 (n=0) , **2** (n=5), **3** (n=14) and **4** (n=15)

Figure 1.3 Nuetral structure of polyoxo derivatives of salen

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

1.2 Species of Salen and Their Related Complexes

The nuetral molecule of salen symbolized as LH_2 is composed of two hydroxyl proton (H_{OH}). In basic solution, nuetral molecule of salen has been able to release two hydroxyl protons and become LH^- and L^{2-} species, respectively. On the other hand, LH_2 species can be protonated by two protons in acidic solution of protic solvent and form LH_3^+ and LH_4^{2+} species, respectively. Species of salen depends on pH of protic solution. Therefore, pH dependence of salen species is shown in following diagram :

$$LH_4^{2+} \xrightarrow{-H^+} LH_3^{+} \xrightarrow{-H^+} LH_2 \xrightarrow{-H^+} LH^{-} \xrightarrow{-H^+} L^{2-}$$

$$\xrightarrow[\text{pH}]{\hspace{12cm}}$$

Equilibrium constants between related species of salen and proton can be writen as following equations.

$$K_1 \quad : \quad L^{2-} + H^+ \rightleftharpoons LH^- \qquad (1.1)$$

$$K_2 \quad : \quad LH^- + H^+ \rightleftharpoons LH_2 \qquad (1.2)$$

$$K_3 \quad : \quad LH_2 + H^+ \rightleftharpoons LH_3^+ \qquad (1.3)$$

$$K_4 \quad : \quad LH_3^+ + H^+ \rightleftharpoons LH_4^{2+} \qquad (1.4)$$

Complexes formation of salen and transition metal cations such as Co(salen) has been shown that salen as L^{2-} species forms complex with Co^{2+} ion as shown in Figure 1.4. Complexation equilibrium of L^{2-} species and divalent cation can be writen below.

$$\beta_{ML} \quad : \quad L^{2-} + M^{2+} \rightleftharpoons ML \qquad (1.5)$$

However, complexation between species of salen and divalent cations can form various complexes depending on the salen and proton.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

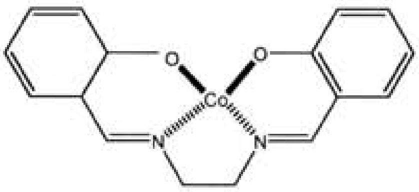


Figure 1.4 A structure of Co(salen) known as saldomine

1.3 Objective and Scope of the Research

Structural conformation of compounds **1**, **2**, **3** and **4** are determined by quantum chemical calculations using semiempirical and ab initio methods. The stabilization energies of optimized structure of related species will be evaluated by ab initio method with extended basis set. The most possible of protonation pathway for each conformations of **1**, **2**, **3** and **4** will be studied. The basicity constants of each conformations for **4** will be determined by potentiometric titration. Complex formation of possible conformation of salens and transition metals will be investigated. Species distribution of compound **4** over the varied pH values will be obtained. Complex formation and stabilities of complex between salen **4** and metal cations nickel(II), copper(II) and zinc(II) will be evaluated by ultraviolet spectroscopic and potentiometric titrations. In addition, the knowledge of this research may lead to make the new catalysts for using in the future.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER II

THEORY

2.1 Equilibrium, Potentiometry and UV-Spectrophotometry

2.1.1 Equilibrium Constant

2.1.1.1 Equilibrium Concentration Constant

An equilibrium constant is a quotient involving the concentrations or activities of reacting species in solution at equilibrium. Generally it is defined as the ratio of the product of the activities *a* of the reaction products, raised to appropriate power, to the products of the activities of the 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.

$$aA + bB \rightleftharpoons cC + dD \qquad K_{eq} = \frac{a_C^c \; a_D^d}{a_A^a \; a_B^b} \tag{2.1}$$

The determination of the activities of complex ionic species at both infinite solution and in real solution is a complicated and time-consuming task. However concentrations are related to activities by the expression

$$a_X = [X]\,\gamma_X \tag{2.2}$$

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 coefficients, based on the Debye-Huckel approach and its extensions, 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.

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

หอสมุดกลาง สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

where[A] indicates molar concentrations. If now it is possible to ensure that the term $\frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b}$ remains constant then the term $\frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} \cdot K_{eq}$ 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 $\frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b}$ in equation (2.3) may be maintained effectively constant by having a large excess of an inert background electrolyte present and using only low concentrations of the reacting ionic species so that any change in their concentrations as a result of their reaction together has an insignificant 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 coefficients 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 coefficients depend on the electrolyte. Consequently, of course, in comparing stoichiometric equilibrium constants, only data obtained under very similar conditions should be used unless the differences between the equilibrium constants are large.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

2.1.1.2 Acidity and Basicity Constants

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

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

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

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

: : :

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

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

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

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

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

: : :

$$L + nH \rightleftharpoons LH_n \quad : \quad \beta_n = \frac{[LH_n]}{[L][H]^n} \tag{2.12}$$

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

The K_i's are called the stepwise protonation constants and the β_i's are called the overall or cumulative protonation constants.

2.2 Method of Calculations

2.2.1 Linear Method, Errors and Statistics

Stability constants are not directly measurable but must be calculated from an observed response function of a fixed, but experimentally adjustable, variable. Since the response data are subject to random error and indeed may be subject to systematic errors if we have not controlled the experiment well, the stability constants will be calculated with limited precision. However, it is important to estimate the precision of any calculated constants, as it will indicate the reliability of the value obtained and in turn the efficiency of the experiment. In addition we need to have a mathematical model for describing the data.

2.2.2 Model Building

Experiments attempts to find some functional form for the way quantities in nature are related. We try to build up a mathematical model which may be an assumed one, in which case we need to measure of how good the model is in describing our data, or it may be derived from first principles and then tested experimentally. The model could be an approximated one, which initially may be acceptable and then refined or modified in the further experimental observations. The typical experiment consists of fixing one group of known values variables called independent variables and then making observations of another dependent variables. In stability constant work, the independent variables might be temperature, ionic strength, or the concentration of one or more components and dependent variables might be e.m.f. or pH or absorbance of the solution. We then calculate or estimate the parameters of interest from the assumed function by relating the dependent to the independent variables.

The parameters for our model are calculated by fitting them to the experimental data. This may be done either graphically or by a mathematical procedure, such as least-squares. The latter calculates the values of the parameters which sum of the squares of the residuals is defined as the difference between the observed and calculated data points at each fixed minimum value of the independent variable. In addition the method of least-squares allows us to obtain the estimated errors of the interested parameters and to estimate the 'goodness of fit' of the assumed model, that is, it allows us to test alternative hypotheses.

2.2.3 Random Errors

Random or observational errors are assumed to follow a Gaussian or normal distribution , expressed mathematically as

$$f\,(r_x) \;=\; \frac{1}{\sqrt{2}\sigma_x}\, e^{-r_x^2/2\sigma_x^2} \tag{2.13}$$

where r_x is the residual of x or observed value - true value , σ_x^2 is the variance of x and σ_x is the standard deviation. The probability of observing the i th residual, P_i in the region r_{xi} to r_{xi} +dr_{xi} is:

$$dP_i \;=\; \frac{1}{\sqrt{2}\sigma_x}\; e^{-r_{xi}^2/2\sigma_x^2}\; dr_{xi} \tag{2.14}$$

Now the probability for a given set of n observations, where P is the product of the probabilities of i th measurements is

$$dP = \prod_{i=1}^{i=n} dP_i = \prod_{i=1}^{i=n} \left(\frac{d\ r_{xi}}{\sqrt{2}\ \sigma_x}\right) e^{\left\{\frac{1}{2\sigma_x^2}\right\}\Sigma r_{xi}^2} \tag{2.15}$$

Based on the statistical principle of maximum likelihood this probability becomes a maximum when the sum of the squares residuals is a minimum.

$$\sum_{i=1}^{n} r_{xi}^2 \;=\; \text{minimum} \tag{2.16}$$

Hence the origin of the term 'least squares ' is apparent.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

The discussion so far has assumed that the measurements of x have all come from the same population distribution, that is, the variance of the residuals are equal. If this is not so, equation (2.14) should be rewritten as :

$$d P_i = \frac{1}{\sqrt{2}\sigma_{xi}} e^{-r_{xi}^2 / 2 \sigma_{xi}^2} dr \tag{2.17}$$

and the equation (2.58) becomes

$$dP = \prod_{i=1}^{i=n} dp_i = \prod_{i=1}^{i=n} \left(\frac{d\, r_{xi}}{\sqrt{2}\, \sigma_{xi}} \right) e^{-\frac{1}{2}\sum\left(r_{xi}^2 / \sigma_{xi}^2 \right)} \tag{2.18}$$

and the least-squares principle gives:

$$\sum_{i=1}^{i=n} \left(\frac{r_{xi}^2}{\sigma_{xi}^2} \right) = \text{minimum} \tag{2.19}$$

A quantity inversely proportional to the variance is termed the weight of an observation. Hence:

$$w_{xi} = \frac{\sigma_0^2}{\sigma_{xi}^2} \tag{2.20}$$

where σ_o^2 is known as the variance of an observation of unit weight. In practice σ_o^2 will often have the value of unity. The quantity now to be minimized is the sum of the weighted squares of the residuals.

$$\sum_{i=1}^{i=n} w_{xi}\, r_{xi}^2 = \text{minimum} \tag{2.21}$$

In practice we cannot know the true value of x , but the principle of least-squares attempts to adjust the estimate of x according to equation (2.21). Generally

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

the experimental data are function of the parameter x so that r_{xi} in equation (2.21) is defined as:

$$r_{xi} = \left[f(x_i) - f(\bar{x})\right] \tag{2.22}$$

and $\bar{x}$ is the least-squares estimator of the true value of the parameter.

2.2.4 Non-Linear Parameter Estimation

2.2.4.1 Least -squares-extension case

To extend least-squares theory to the non-linear case [12], that is the situation where the dependent variables are non-linear functions of the independent variables, we take equation and express the dependent variables as a function of the unknowns by a Taylor series expansion. Thus if the initial estimates of the parameter values are $\left(x_1^0\, x_2^0 \ldots x_m^0\right)$ then the observables are expressed about this point in parameter space by:

$$o_i = f_i\left(x_1^o \ldots x_m^0\right) + \left(\frac{\partial f_i}{\partial x_i}\right)_0 \left(x_1 - x_1^o\right) + \ldots + \left(\frac{\partial f_i}{\partial x_m}\right)_0 \left(x_m - x_m^o\right) \tag{2.23}$$

that is

$$o_i = f_i\left(x_1^o \ldots x_m^0\right) + \sum_{j=1}^{j=m} \left(\frac{\partial f_i}{\partial x_j}\right)_0 \Delta x_j \tag{2.24}$$

where terms higher than first order have been neglected. Therefore the change in the observables Δo_i on making the corrections Δx_j are given by

$$\Delta o_i = o_i - f_i\left(x_1^o \ldots x_m^0\right) = \sum_{j=1}^{j=m} \left(\frac{\partial f_i}{\partial x_j}\right)_0 \Delta x_j \tag{2.25}$$

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

2.2.4.2 Hypothesis testing

Another quantity which has been used in non-linear estimation situations is the Halmilton *R*-factor. In this procedure the *R*-factor defined by :

$$R = \left[\frac{\sum_{i=1}^{i=n} w_i \left(o_i^{\text{calc}} - o_i^{\text{obs}} \right)^2}{\sum_{i=1}^{i=n} w_i \left(o_i^{\text{obs}} \right)^2} \right]^{\frac{1}{2}} \tag{2.26}$$

is compared with R_{lim} calculated from :

$$R_{\text{lim}} = \left[\frac{\sum_{i=1}^{i=n} w_i \; e_i^2}{\sum_{i=1}^{i=n} w_i \left(o_i^{\text{obs}} \right)^2} \right]^{\frac{1}{2}} \tag{2.27}$$

where e_i is the residual in the *i* th equation calculated from the estimated errors in all the experimental quantities using error propagation rules, o_i^{calc} and o_i^{obs} are the calculated and the observed values of the response variable respectively, w_i are the appropriate weighting factors. A satisfactory fit is assumed if $R < R_{\text{lim}}$.

2.3 Equilibrium Constants by Potentiometry

The acidity and basicity constants were calculated by fitting the pH data to the SUPERQUAD program [13] which has been widely used to calculate the equilibrium constants of many ligands in solution. The formation constants are determined by minimization of an error-square sum based on measure electrode potentials. The SUPERQUAD program also permits refinement of any reactant concentration or standard electrode potential. The refinement is incorporated into 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... in the solution equilibria, there is a chemical constant, the formation constant, which is expressed as a concentration quotient in equation (2.28).

$$\beta_{ab}\ldots = \frac{[A_aB_b\ldots]}{[A]^a[B]^b\ldots} \qquad (2.28)$$

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 (2.29), where [A] is the concentration of the electro-active ion.

$$E = E^{\circ} + S_L \log [A] \qquad (2.29)$$

E is the measured potential, and E^0 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^0 and S_L are usually obtained in a separate calibration experiment. Further there is a modified Nernst equation.

$$E = E^{\circ} + S_L \log [H^+] + r\,[H^+] + s\,[H^-]^{-1} \qquad (2.30)$$

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 weightings and dilutions, standardization of reagents (use of carbonate-free alkali in particular),

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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 trends.

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

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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.

$$A = \varepsilon c l \tag{2.31}$$

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.

$$A_{obs}^{\lambda} = \varepsilon_1^{\lambda} c_1 + \varepsilon_2^{\lambda} c_2 + \ldots\ \varepsilon_n^{\lambda} c_n \tag{2.32}$$

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 Spectroscopic Data

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

$$M + L \xrightleftharpoons{K_1} ML \tag{2.33}$$

$$ML + L \xrightleftharpoons{K_2} ML_2 \tag{2.34}$$

$$ML_{n-1} + L \xrightleftharpoons{K_n} ML_n \tag{2.35}$$

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

$$[M]_T = [M] + [ML] + [ML_2] + \ldots\ [ML_n] \tag{2.36}$$

$$[L]_T = [L] + [ML] + 2[ML_2] + \ldots\ n[ML_n] \tag{2.37}$$

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

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

$$\bar{n} = \frac{\text{total bound ligand}}{\text{total metal}} = \frac{[L]_T - [L]}{[M]_T} \tag{2.38}$$

Substituting Equation (2.36) and (2.37) in (2.38) yields

$$\bar{n} = \frac{[ML]+2[ML_2]+...n[ML_n]}{[M]+[ML]+[ML_2]+...[ML_n]} \tag{2.39}$$

In summation terms equation (2.39) becomes

$$\bar{n} = \frac{\sum_{i=1}^{i=n} i[ML_i]}{[M] + \sum_{i=1}^{i=n} [ML_i]} \tag{2.40}$$

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

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \tag{2.41}$$

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \tag{2.42}$$

Combining equation (2.42) into (2.40) gives

$$\bar{n} = \frac{\sum_{i=1}^{i=n} i\beta_i[L]^i}{1 + \sum_{i=1}^{i=n} [L]^i} \tag{2.43}$$

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.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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

$$\varepsilon_{obs}^{\lambda} = \frac{A_{obs}^{\lambda} - \varepsilon_{L}^{\lambda}[L]_T}{[M]_T} \tag{2.44}$$

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

$$A_{obs}^{\lambda} = \varepsilon_{M}^{\lambda}[M] + \sum_{i=1}^{i=n}\left(\varepsilon_{i}^{\lambda}[ML_i]\right) + \varepsilon_{L}^{\lambda}[L] \tag{2.45}$$

Where $\varepsilon_{M}^{\lambda}$, $\varepsilon_{L}^{\lambda}$ and $\varepsilon_{i}^{\lambda}$ are the molar absorptivities of the metal, ligand and complexes ML_i at wavelength λ. Substituting (2.45) in (2.44) gives,

$$\varepsilon_{obs}^{\lambda} = \frac{\varepsilon_{M}^{\lambda}[M] + \sum_{i=1}^{i=n}(\varepsilon_{i}^{\lambda}[ML_i]) - \varepsilon_{L}^{\lambda}([L]_T - [L])}{[M]_T} \tag{2.46}$$

and from equation (2.37),

$$\varepsilon_{obs}^{\lambda} = \frac{\varepsilon_{M}^{\lambda}[M] + \sum_{i=1}^{i=n}(\varepsilon_{i}^{\lambda}[ML_i]) - \sum_{i=1}^{i=n}(\varepsilon_{L}^{\lambda}\, i[ML_i]^{i})}{[M]_T} \tag{2.47}$$

Substituting , equation (2.42) to (2.47) gives

$$\varepsilon_{obs}^{\lambda} = \frac{\varepsilon_{M}^{\lambda}[M] + \sum_{i=1}^{i=n}(\varepsilon_{i}^{\lambda}\,\beta_i[M][L]^{i} - i\varepsilon_{L}^{\lambda}\,\beta_i[M][L]^{i})}{[M]_T} \tag{2.48}$$

Dividing through by [M] results

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

$$\varepsilon_{obs}^{\lambda} = \frac{\varepsilon_{M}^{\lambda} + \sum_{i=1}^{i=n}(\varepsilon_{i}^{\lambda} - i\,\varepsilon_{L}^{\lambda})\beta_{i}[L]^{i}}{[M]_{T}/[M]} \qquad (2.49)$$

From equation (2.36) and (2.42)

$$\varepsilon_{obs}^{\lambda} = \frac{\varepsilon_{M}^{\lambda} + \sum_{i=1}^{i=n}(\varepsilon_{i}^{\lambda} - i\,\varepsilon_{L}^{\lambda})\beta_{i}[L]^{i}}{1 + \sum_{i=1}^{i=n}\beta_{i}[L]^{i}} \qquad (2.50)$$

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 (2.42). It follows that solutions having the same value of $\varepsilon_{obs}^{\lambda}$ must have the same value for [L]. Sinc $\bar{n}$ is a function of [L] only, it also follows that these solutions have the same value of $\bar{n}$.

From Equation (2.38),

$$[L]_T = [L] + \bar{n}[M]_T \qquad (2.51)$$

and for a constant value of [L] this is a linear equation whose slope is and intercept [L].

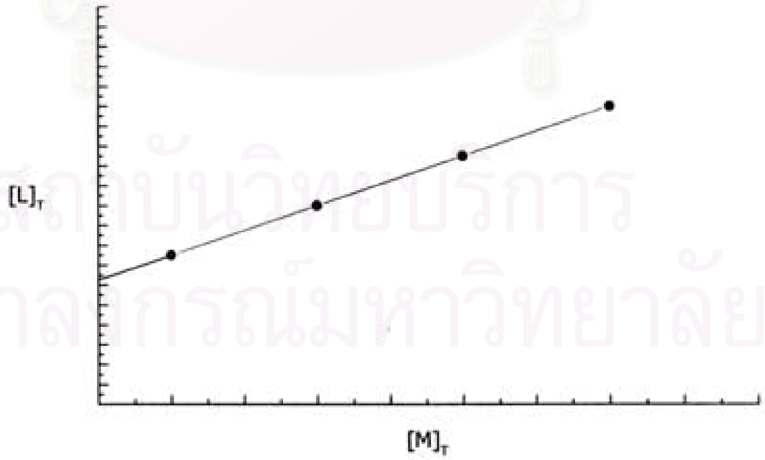


Figure 2.1 Corresponding solution of $[L]_T$ against $[M]_T$ for a series of solutions having the same value of $\varepsilon_{obs}^{\lambda}$

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

2.5 Inert Background Electrolyte

To study acid-base characteristics of ligand and their complexation properties toward metal, ionic strength is 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 electrolyte 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 is to keep the overall ionic strength and activity coefficient constant. Properties of the chosen inert background electrolyte 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 and 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.

Inert background electrolytes that are commonly used in aqueous solvent are sodium salts such as the perchlorate or nitrate e.g. sodium perchlorate ($NaClO_4$), sodium nitrate ($NaNO_3$), perchlorate is usually more suitable than any other ions. Sodium chloride (NaCl) has been used as an inert background electrolyte, but its use is less common than perchlorate or nitrate because chloride ions often form complexes with metal ions under study. Potassium salts such as potassium nitrate (KNO_3) and potassium chloride (KCl) have also been used occasionally, but potassium perchlorate ($KClO_4$) is unsuitable due to its low solubility in water [12].

In non-aqueous electrolyte e.g. methanolic and ethanolic solutions, quaternary ammonium salts of perchlorate , chloride, nitrate or trifate such as tetraethylammonium perchlorate (EtN_4ClO_4), tetramethylammonium chloride (MeN_4Cl) and tetrabuthylammonium trifluoromethanesulfonate ($BuN_4CF_3SO_3$) are usually supplied. It is found that MeN_4Cl is not suitable for investigation of complex formation in the methanolic solution, because chloride can easily form complex(es) with many metal ions. The background electrolytes for basicity study of the ligands and their complexation in the ethanolic solution is tetramethylammonium nitrate (MeN_4NO_3). For many equilibrium studies of the ligands and their complexes with metal ions in acetonitrile solution, the MeN_4ClO_4 and BuN_4ClO_4 are suitable background electrolytes.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

หอสมุดกลาง สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

2.6 Quantum Chemical Calculations

2.6.1 Schrödinger equation

The Schrödinger equation can be solved exactly for only a few problems, such as a particle in a box, the harmonic oscillator, the particle on a ring, the particle on a sphere and the hydrogen atom. A common feature of these problems is that it is necessary to impose certain requirements (often called boundary conditions) on possible solutions to the equation. Thus, for a particle in a box with infinitely high walls, the wavefunction is required to go to zero at the boundaries. For a particle on a ring the wavefunction must have a periodicity of 2π because it must repeat every traversal of the ring. An additional requirement on solutions to the Schrödinger equation is that the wavefunction at a point r when multiplied by its complex conjugate is the probability of finding the particle at the point (this is the Born interpretation of the wavefunction). The square of an electronic wavefunction thus gives the electron density at any given point. If we integrate the probability of finding the particle over all space, then the result must be one as the particle must be somewhere:

$$\int \Psi^* \Psi d\tau = 1 \tag{2.52}$$

Indicates that the integration is over all space. Wavefunctions which satisfy this condition are said to be normalised. It is usual to require the solutions to the Schrödinger equation to be orthogonal:

$$\int \Psi_m^* \Psi_n d\tau = 0 \ (m \neq n) \tag{2.53}$$

A convenient way to express both the orthogonality of different wavefunctions and the normalisation conditions uses the Kronecker delta:

$$\int \Psi_m^* \Psi_n d\tau = \delta_{mn} \tag{2.54}$$

When used in this context, the Kronecker delta can be taken to have a value of one if m equals n and zero otherwise. Wavefunctions that are both orthogonal and normalised are said to be orthonormal.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

2.6.2 The Born-Oppenheimer approximation

It was stated above that the Schrödinger equation can not be solved exactly for any molecular systems. However, it is possible to solve the equation exactly for the simplest molecular species, H_2^+ (and isotopically equivalent species such as HD^+), when the motion of the electrons is decoupled from the motion of the nuclei in accordance with the Born-Oppenheimer approximation. The masses of the nuclei are much greater than the masses of the electrons (the resting mass of the lightest nucleus, the proton, is 1836 times heavier than the resting mass of the electron). This means that the electrons can adjust almost instantaneously to any changes in the positions of the nuclei. The electronic wavefunction thus depends only on the positions of the nuclei and not on their momenta. Under the Born-Oppenheimer approximation the total wavefunction for the molecule can be written in the following form:

$$\Psi_{tot}(\text{nuclei,electrons}) = \Psi(\text{electrons})\,\Psi(\text{nuclei}) \tag{2.55}$$

The total energy equals the sum of the nuclear energy (the electrostatic repulsion between the positively charged nuclei) and the electronic energy. The electronic energy comprises the kinetic and potential energy of the electrons moving in the electrostatic field of the nuclei, together with electron-electron repulsion: $E_{tot} = E(\text{electrons}) + E(\text{nuclei})$.

When the Born-Oppenheimer approximation is used we concentrate on the electronic motions; the nuclei are considered to be fixed. For each arrangement of the nuclei the Schrödinger equation is solved for the electrons alone in the field of the nuclei. If it is desired to change the nuclear positions then it is necessary to add the nuclear repulsion to the electronic energy in order to calculate the total energy of the configuration.

2.6.3 Ab Initio Hartree-Fock Methods

The Hartree-Fock equations are usually solved in different ways for atoms and for molecules. For atoms, the equations can be solved numerically if it is assumed that the electron distribution is spherically symmetrical. However, these numerical solutions are not particularly useful. Fortunately, analytical approximations to these solutions, which are very similar to those obtained for the hydrogen atom, can be used with considerable success. These approximate analytical functions thus have the form:

$$\psi = R_{nl}(r)\,Y_{lm}(\theta,\phi) \tag{2.56}$$

Y is a spherical harmonic (as for the hydrogen atom) and R is a radial function. The radial functions obtained for the hydrogen atom cannot be used directly for polyelectronic atoms due to the screening of the nuclear charge by the inner shell electrons, but the hydrogen atom functions are acceptable if the orbital exponent is adjusted to account for the screening effect. Even so, the hydrogen atom functions are not particularly convenient to use in molecular orbital calculations due to their complicated functional form. Slater suggested a simpler analytical form for the radial functions:

$$R_{nl}(r) = (2\zeta)^{n+\frac{1}{2}}\left[(2n)!\right]^{-\frac{1}{2}} r^{n-1} e^{-\zeta r} \tag{2.57}$$

These functions are universally known as Slater-type orbitals (STOs) and are just the leading term in the appropriate Lagrange's polynomials. The first three Slater functions are as follows:

$$R_{1s}(r) = 2\zeta^{\frac{3}{2}} e^{-\zeta r} \tag{2.58}$$

$$R_{2s}(r) = R_{2p}(r) = \left(\frac{4\zeta^5}{3}\right)^{\frac{1}{2}} r e^{-\zeta r} \tag{2.59}$$

$$R_{3s}(r) = R_{3p}(r) = R_{3d}(r) = \left(\frac{8\zeta^7}{45}\right)^{\frac{1}{2}} r^2 e^{-\zeta r} \tag{2.60}$$

To obtain the whole orbital we must multiply R(r) by the appropriate angular part. For example, we would use the following expressions for the I s, 2s and 2p, orbitals:

$$\phi_{1s}(r) = \sqrt{(\zeta^3/\pi)\exp(-\zeta r)} \tag{2.61}$$

$$\phi_{2s}(r) = \sqrt{(\zeta^5/3\pi)r\exp(-\zeta r)} \tag{2.62}$$

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

$$\phi_{2p_z}(r) = \sqrt{(\zeta^5/\pi)\exp(-\zeta r)\cos\theta} \qquad (2.63)$$

Slater provided a series of empirical rules for choosing the orbital exponents ζ, which are given by:

$$\zeta = \frac{Z-\sigma}{n^*} \qquad (2.64)$$

Z is the atomic number and a is a *shielding constant*, determined as below. *n** is an effective principal quantum number which takes the same value as the true principal quantum number for n = 1, 2 or 3, but for n = 4, 5, 6 has the values 3.7, 4.0, 4.2 respectively. The shielding constant is obtained as follows:

First divide the orbitals into the following groups:

(1s); (2s, 2p); (3s, 3p); (3d); (4s, 4p); (4d); (4f); (5s, 5p); (5d)

For a given orbital, a is obtained by adding together the following contributions:

(a) zero from an orbital further from the nucleus than those in the group;

(b) 0.35 from each other electron in the same group, but if the other orbital is the 1s then the contribution is 0.3;

(c) 1.0 for each electron in a group with a principal quantum number 2 or more fewer than the current orbital;

(d) for each electron with a principal quantum number 1 fewer than the current orbital: 1.0 if the current orbital is d or f; 0.85 if the current orbital is s or p.

The shielding constant for the valence electrons of silicon is obtained using Slater's rules as follows. The electronic configuration of Si is ($1s^2$)($2S^2$ $2P^6$) ($3S^2$ $3p^2$). We therefore count 3 x 0.35 under rule (b), 2.0 under rule (c), and 8 x 0.85 under rule (d), giving a total of 9.85. When subtracted from the atomic number (14) this gives 4.15 for the value of Z -σ.

Direct solution of the Hartree-Fock equations is not a practical proposition for molecules and so it is necessary to adopt an alternative approach. The most popular strategy is to write each spin orbital as a linear combination of single electron orbitals:

$$\psi_i = \sum_{v=1}^{K} c_{vi}\phi_v \qquad (2.65)$$

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

The one-electron orbitals ϕ_v are commonly called basis functions and often correspond to the atomic orbitals. We will label the basis functions with the Greek letters μ, ν, λ and σ. In the case of equation (2.65) there are **K** basis functions and we should therefore expect to derive a total of **K** molecular orbitals (although not all of these will necessary be occupied by electrons). The smallest number of basis functions for a molecular system will be that which can just accommodate all the electrons in the molecule. More sophisticated calculations use more basis functions than a minimal set. At the Hartree-Fock limit the energy of the system can be reduced no further by the addition of any more basis functions; however, it may be possible to lower the energy below the Hartree-Fock limit by using a functional form of the wavefunction that is more extensive than the single Slater determinant.

In accordance with the variation theorem we require the set of coefficients c_{vi} that gives the lowest energy wavefunction, and some scheme for changing the coefficients to derive that wavefunction. For a given basis set and a given functional form of the wavefunction (i.e. a Slater determinant) the best set of coefficients is that for which the energy is a minimum, at which point

$$\frac{\partial E}{\partial c_{vi} = 0}$$

for all coefficients c_{vi}. The objective is thus to determine the set of coefficients that gives the lowest energy for the system.

The Fock matrix is a K x K square matrix that is symmetric if real basis functions are used. The Roothaan-Hall equations can be conveniently written as a matrix equation:

$$\mathbf{FC} = \mathbf{SCE} \qquad (2.66)$$

The elements of the K x K matrix C are the coefficients c_{vi} :

$$C = \begin{pmatrix} c_{1,1} & c_{1,2} & \cdots & c_{1,K} \\ c_{2,1} & c_{2,2} & \cdots & c_{2,K} \\ \vdots & \vdots & & \vdots \\ c_{K,1} & c_{K,2} & \cdots & c_{K,K} \end{pmatrix} \qquad (2.67)$$

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

E is a diagonal matrix whose elements are the orbital energies:

$$E = \begin{pmatrix} \varepsilon_1 & 0 & \dots & 0 \\ 0 & \varepsilon_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \varepsilon_K \end{pmatrix} \qquad (2.68)$$

Let us consider how we might solve the Roothaan-Hall equations and thereby obtain the molecular orbitals. The first point we must note is that the elements of the Fock matrix, which appear on the left hand side of equation (2.66), depend on the molecular orbital coefficients $c_{\nu i}$, which also appear on the right-hand side of the equation. Thus an iterative procedure is required to find a solution. The one-electron contributions $H_{\mu\nu i}^{core}$ due to the electrons moving in the field of the bare nuclei do not depend on the basis set coefficients and remain unchanged throughout the calculation. However, the Coulomb and exchange contributions do depend on the coefficients and we would expect these to vary throughout the calculation. The individual two-electron integrals $(\mu\nu|\lambda\sigma)$ are, however, constant throughout the calculation. An obvious strategy is thus to calculate and store these integrals for later use.

Having written the Roothaan-Hall equations in matrix form we would obviously like to solve them using standard matrix eigenvalue. However, standard eigenvalue methods would require an equation of the form FC = CE. The Roothaan-Hall equations only adopt such a form if the overlap matrix, S, is equal to the unit matrix, I (in which all diagonal elements are equal to 1 and all off-diagonal elements are zero). The functions ϕ are usually normalised but they are not necessarily orthogonal (for example, because they are located on different atoms) and so there will invariably be non- zero off-diagonal elements of the overlap matrix. To solve the Roothaan-Hall equations using standard methods they must be transformed. This corresponds to transforming the basis functions so that they form an orthonorinal set. A matrix X is determined by an equation, such that $X^TSX = I$. X^T is the transpose of X, obtained by interchanging rows and columns. There are various ways in which X can be calculated; in symmetric orthogonalisation, the overlap matrix is diagonalised. Diagonalisation involves finding the matrix U such that

$$\mathbf{U}^{\mathrm{T}}\mathbf{S}\mathbf{U} = \boldsymbol{D} = diag(\lambda_1 \ldots \lambda_K) \tag{2.69}$$

D is the diagonal matrix containing the eigenvalues λ_i of S, and U contains the eigenvectors of S. U^T is the transpose of the matrix U. (This expression is often written U^{-1} SU = D since for real basis functions $U^{-1} = U^T$.) Then the matrix X is given by $X = UD^{-1/2}U^T$ where, $D^{-1/2}$ is formed from the inverse square roots of D. We shall write X as $S^{-1/2}$, as it can be considered to be the inverse square root of the overlap matrix: $S^{-1/2}SS^{-1/2} = I$.

The Roothaan-Hall equations can now be manipulated as follows. Both sides of equation (2.66) are pre-multiplied by the matrix $S^{-1/2}$:

$$\boldsymbol{S^{-1/2}FC = S^{-1/2}SCE = S^{1/2}CE} \tag{2.70}$$

Inserting the unit matrix, in the form $S^{-1/2}S^{1/2}$ into the left-hand side gives:

$$\boldsymbol{S^{-1/2}F\left(S^{-1/2}S^{1/2}\right)C = S^{1/2}CE} \tag{2.71}$$

or

$$\boldsymbol{S^{-1/2}FS^{-1/2}\left(S^{1/2}C\right) = \left(S^{1/2}C\right)E} \tag{2.72}$$

Equation (2.72) can be written F'C'=C'E, where $F' = S^{-1/2}FS^{-1/2}$ and $C' = S^{1/2}C$.

The matrix equation F'C'=C'E can be solved using standard methods; a solution only exists if the determinant |F' - EI| equals zero. In simple cases this can be done by multiplying out the determinant to give a polynomial (the secular equation) whose roots are the eigenvalues ε_i, but for large matrices a much more practical approach involves the diagonalisation of F'. The matrix of coefficients, C', are the eigenvectors of F. The basis function coefficients C can then be obtained from C' using $C=S^{-1/2}C'$. A common scheme for solving the Roothaan-Hall equations is thus as follows:

1. Calculate the integrals to form the Fock matrix, F.
2. Calculate the overlap matrix, S.
3. Diagonalise S.
4. Form $S^{-1/2}$.
5. Guess, or otherwise calculate an initial density matrix, P.
6. Form the Fock matrix using the integrals and the density matrix P.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

หอสมุดกลาง สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

7. Form $F' = S^{-1/2}FS^{-1/2}$.
8. Solve the secular equation $|F' - EI| = 0$ to give the eigenvalues E and the eigenvectors C' by diagonalising F'.
9. Calculate the molecular orbital coefficients, C from $C = S^{-1/2}C'$.
10. Calculate a new density matrix, P, from the matrix C.
11. Cheek for convergence. If the calculation has converged, stop. Otherwise repeat from step 6 using the new density matrix P.

This procedure requires an initial guess of the density matrix, P. The simplest approach is to use the null matrix, which corresponds to ignoring all the electron-electron terms so that the electrons just experience the bare nuclei. This can sometimes lead to convergence problems which may be prevented if a lower level of theory (such as semi-empirical or extended Hückel) is used to provide the initial guess. Moreover, a better guess may enable the calculation to be performed more quickly. A variety of criteria can be used to establish whether the calculation has converged or not. For example, the density matrix can be compared with that from the previous iteration, and/or the change in energy can be monitored together with the basis set coefficients.

The result of a Hartree-Fock calculation is a set of K molecular orbitals where K is the number of basis functions in the calculation. The N electrons are then fed into these orbitals in accordance with the Aufbau principle, two electrons per orbital, starting with the lowest energy orbitals. The remaining orbitals do not contain any electrons; these are known as the virtual orbitals. Alternative electronic configurations can be generated by exciting electrons from the occupied orbitals to the virtual orbitals.

A Hartree-Fock calculation provides a set of orbital energies, Φ_i.The energy of an electron in a spin orbital is calculated by adding the core interaction $H_{\mu\nu}^{core}$ to the Coulomb (J_{ij}) and exchange interactions (K_{ij}) with the other electrons in the system:

$$\varepsilon_i = H_{ii}^{core} + \sum_{j=1}^{N/2} \left(2J_{ij} - K_{ij}\right) \tag{2.73}$$

The total electronic energy of the ground state is given by equation (2.82):

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

$$E = 2\sum_{i=1}^{N/2} \mathrm{H}_{ii}^{core} + \sum_{i=1}^{N/2}\sum_{j=1}^{N/2}\left(2J_{ij} - K_{ij}\right) \tag{2.74}$$

The total energy is therefore not equal to the sum of the individual orbital energies, but is related as follows:

$$E = \sum_{i=1}^{N} \varepsilon_i - \sum_{i=1}^{N/2}\sum_{j=1}^{N/2}\left(2J_{ij} - K_{ij}\right) \tag{2.75}$$

The reason for the discrepancy is that the individual orbital energies include contributions from the interaction between that electron and all the nuclei and all other electrons in the system. The Coulomb and exchange interactions between pairs of electrons are therefore counted twice when summing the individual orbital energies.

2.6.4 Basis Set

2.6.4.1 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 quantum mechanical picture, electrons have a finite probability of existing anywhere in space; this limit corresponds to the infinite basis set. Standard basis sets for electronic structure calculations use linear combinations of gaussian functions to form the orbitals. Gaussain (program) offers a wide range of per-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.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

2.6.4.2 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 [14] 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.

2.6.4.3 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 3-21G [15-20] and 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 orbtals 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], use three sizes of contracted functions for each orbital-type.

2.6.4.4 Polarized Basis Sets.

Split valence basis sets allow orbitals to change size, but not of change shape. Polarized basis sets remove this limitation by adding orbitals with angular momentum beyond what is required for the ground state to the description of each atom. For example, polarized basis sets add d functions to carbon atoms and f functions to transition metals, and some of them add p functions to hydrogen atoms. So far, the only polarized basis set we've used is 6-31G(d). Its name indicates that it is the 6-31G basis set with d functions added to heavy atoms. This basis set is becoming very common for calculations involving up to medium-sized systems. This basis set is also known as 6-31G*. Another popular polarized basis set is 6-31G(d,p), also known as 6-31G**, which adds p functions to hydrogen atoms in addition to the d functions on heavy atoms.

2.6.4.5 Diffuse Functions.

Diffuse functions are large-size versions of s- and p-type functions (as oppose to the standard valence-size functions). They allow orbitals to occupy a larger region of space. Basis sets with diffuse functions are important for systems where electrons are relatively far from the nucleus: molecules with lone pairs, anions and other systems with significant negative charge, systems in their excited states, systems with low ionization potentials, descriptions of absolute acidities, and so on. The 6-31+G(d) basis set is the 6-31G(d) basis set with diffuse functions added to heavy atoms. The double plus version, 6-31++G(d), adds diffuse functions to the hydrogen atoms as well. Diffuse functions on hydrogen atoms seldom make a significant difference in accuracy.

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 (the "reactants") from that of the dimer (the "product"). 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 [28] in which the entire 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 optimised 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.

2.6.6 Semi-empirical Methods

2.6.6.1 AM1 (Austin Model 1) Method

AM1 [29] 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

$$V_{nn}(A,B) = V_{nn}^{MINDO}(A,B) + \frac{Z'_A\, Z'_B}{R_{AB}} \times \left(\sum_k a_{kA} e^{-b_{kA}(R_{AB}-c_{kA})^2} + \sum_k a_{kB} e^{-b_{kB}(R_{AB}-c_{kB})^2}\right) \tag{2.76}$$

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 [29] 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. In this reparameterization, the AM1 expression for the core-core repulsion, equation (2.74), was kept, except that only 2 Gaussians were assigned to each atom. These Gaussian parameters were included as an integral part of the model, and allowed to vary freely.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER III

EXPERIMENTAL

3.1 Chemicals and Equipment

3.1.1 Chemicals

▪ Potassium nitrate	Electrochemical grad, Fluka, Germany
▪ Sodium hydroxide solution1.0 M	Titrisol, Merck, Germany
▪ Hydrochloric acid solution1.0 M	Titrisol, Merck, Germany
▪ Nitric acid concentrated	Analar grade, Merck, Germany
▪ Cobalt(II) nitrate hexahydrate	Analar grade, Merck, Germany
▪ Nickel(II) nitrate hexahydrate	Analar grade, Merck, Germany
▪ Copper(II) nitrate	Analar grade, Merck, Germany
▪ Zinc(II) nitrate	Analar grade, Merck, Germany
▪ Cadmium(II) nitrate tetrahydrate	Analar grade, Merck, Germany
▪ Potassium hydrogen phthalate	Analar grade, Carlo Erba, Italy
▪ Cobalt(II) perchlorate hexahydrate	Analar grade, Merck, Germany
▪ Nicke;(II) perchlorate hexahydrate	Analar grade, Merck, Germany
▪ Copper(II) trifluoromethanesulfonate	Analar grade, Aldrich, USA
▪ Zinc(II) trifluoromethanesulfonate	Analar grade, Aldrich, USA
▪ Tetrabutyl ammonium trifluoromethanesulfonate	Analar grade, Aldrich, USA
▪ Tetrabutyl ammonium hydroxide	Analar grade, Aldrich, USA
▪ Methanol	Spectro grade, Merck, Germany
▪ Salen	Synthetic ligand
▪ Argon gas	Ultra high purity grade, TGI, Thailand
▪ Buffer pH 4.00	Titrisol, Merck, Germany
▪ Buffer pH 10.00	Titrisol, Merck, Germany

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

3.1.2 Equipments

- Automatic titrator, Mettler, Model DL 25, Switzerland
- Thermostat bath, Model DT-2, Denmark
- Combined pH electrode, Mettler, Model DG 111-SC, Switzerland
- UV-VIS Spectrophotometer, HP, Switzerland.
- Personal Computer IBM 300GL, PII/350, RAM 512 MB
- Magnetic Stirrer
- Micrometer Syringe 2.00 cm^3, GS-1200, Gilmont, USA

3.2 Potentiometry

3.2.1 Preparation of solution

Supporting electrolytes, used in the research, were 0.1 and 0.5 M KNO_3 which obtained by dissolution of a weighed quantity of dried KNO_3, Electrochemical grade, Fluka, in Water. Double distilled deionized water was used in solution preparations. Stock solutions of the ligand **4** used in the titrations was 0.001 M in water with 0.1 and 0.5 M KNO_3. Sodiumhydroxide (NaOH) of which concentration about 0.1 M and o.5 M made by dilution of sodium hydroxide stock solution which ionic strength of 0.1 and 0.5 M KNO_3 were used as the titrant base. The primary standard solution of potassium hydrogen phthalate (KHP) was prepared by dilution of a weighed quantity of dried KHP in water. The stock solution of hydrochloric acid and nitric acid in 0.1 and 0.5 M KNO_3 were prepared from concentrated and standard solution, respectively. The standard buffers pH = 4.00 and pH = 10.00 of Merck were used in calibration of pH electrode. The stock solution of hydrochloric acid and nitric acid were used for preparation of standard solution of 0.1 M HCl and 0.1 M HNO_3 in 0.1 and 0.5 M KNO_3, standardized using 0.1 M NaOH titrant.

The water with 0.1 and 0.5 M KNO_3 of the 0.1 M $Zn(NO_3)_2$ was used in the titration for the complex formation study of the ligand **4**.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

I 20490598

3.2.2 The Calibration of Electrode

An automatic titrator, Mettler DL25 including combined pH electrode of Mettler DG111-SC was used in the titration. The pH electrode was calibrated by standard buffers of pH 4.01 and 10.00, at 25 ± 0.1 °C.

The pH electrode was calibrated using standard buffer pH 4.01 and 10.0. Nernstian slope and isopotential point parameters obtained from electrode calibration were used for correct pH.

The titration were performed under ultrapure argon gas satulated by 0.1 and 0.5 M KNO_3 vapour, through the titration beaker. The titration beaker was kept constantly at 25 °C with deviation of ± 0.1 °C by the external circulation control of thermostat bath. Each titration, at least 50 titrating data were recorded and at least 3 titrations were performed.

3.2.3 Potentiometric Titration

Each titration, 0.001 M of the ligands of **4** in water of 10 cm^3 was used. The titrant base, 0.1 M NaOH in 0.1 and 0.5 M KNO_3 was standardized against the primary standard solution of potassium hydrogen phthalate For standard solution of 0.1 M HNO_3 in 0.1 and 0.5 M KNO_3 was standardized against the titrant base. The standard solution of HCl and HNO_3 were used to adjust the pH of the working solution.

The titrations were performed under ultrapure argon gas, saturated by 0.1 M potassium nitrate vapour, through the titration beaker. The titration beaker was kept constantly at 25 °C with deviation of ± 0.1 °C by the external circulation control of thermostat bath. Each titration, at least 50 titrating data were recorded and at least 3 titrations were carried out.

3.2.4 Evaluation of Titration Data

The basicity constants **4** were evaluated from titration data using computer refinement program. The calculations were performed on the Personal computer IBM

300GL PII/350. The titrating data obtained from the measurements were used in the evaluation and the optimization process by the SUPERQUAD program . The ranges of titration data for the titrations of **4** in 0.1 and 0.5 M KNO_3 are shown in Table 3.1 and 3.2, respectively.

Table 3.1 Titration data range of **4 (L)** in 0.1 M KNO_3 at 25 °C

Titration	Initial Concentration (mM)		pH range	Data point
	L	HNO_3		
1	0.916	9.500	2.23 - 11.59	72
2	0.916	13.635	2.16 – 11.48	68
3	0.877	13.510	2.16 – 10.21	55
4	8.889	13.629	2.06 – 10.55	66

Table 3.2 Titration data range of **4 (L)** in 0.5 M KNO_3 at 25 °C

Titration	Initial Concentration (mM)		pH range	Data point
	L	HCl		
1	0.907	7.745	2.35 – 12.16	53
2	0. 872	7.745	2.84 - 11.27	52
3	0.109	4.900	2.27 – 12.66	64
4	0.105	1.278	4.27 - 11.49	50

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

3.3 UV-VIS Spectrophotometry

3.3.1 Solution and Preparation

Methanolic solution of 0.01 M $Bu_4NCF_3SO_3$ was used as supporting electrolyte. The 0.01 M $Bu_4NCF_3SO_3$ was prepared by dissolution of a weighed amount of dried $Bu_4NCF_3SO_3$ in volumetric flask using methanol as solvent.

Preparation of $1x10^{-5}$ M ligand **4** : A weighed amount of ligand **4** was dissolved in volumetric flask 25 cm^3 using 0.01 M $Bu_4NCF_3SO_3$.

Preparation Metal solutions : Solutions of cobalt(II), nickel(II), copper(II) and zinc(II) in 0.01 M $Bu_4NCF_3SO_3$ were prepared from dried $CoClO_4.6H_2O$, $NiClO_4.6H_2O$, $Cu(CF_3SO_3)_2$, and $Zn(CF_3SO_3)_2$, respectively. The metal ion solutions of $6x10^{-4}$ M and $1x10^{-5}$ M in 0.01 M $Bu_4NCF_3SO_3$ were used in UV-VIS spectrometric titrations.

3.3.2 UV-VIS Spectrometric Titration

As titrand, 3.00 cm^3 of $1x10^{-5}$ M ligand **4** in 0.01 M $Bu_4NCF_3SO_3$ was placed in UV-VIS titrating cell (Cuvet size ca. 4 cm^3) . UV-VIS spectra of titrations were recorded against the supporting electrolyte (0.01 M $Bu_4NCF_3SO_3$). The titration were performed at room temperature, ca. 25 °C. Solution was stirred ca 15 minutes using magnetic stirer before recording its spectra.

Metai ion solution was added 0.05 cm^3 for each titration step from micrometer syringe of size 2.00 cm^3, GS-1200, Gilmont (connected with capillary teflon tube). The maximum volume of titrant is 0.55 cm^3. Each system, at least ten titration steps were performed.

UV-VIS spectra were automatically recorded at wavelength within 190 to 1100 nm step by 1 nm.

3.3.3 Treatment of UV-VIS Spectrometric Data

Absorbances were seleceted from the whol range of UV-VIS spectra. The absorbances at selected wavelengths steping by 10 to 20 nm were collected for at least ten different number of wavelength. The stability constants of complexes between lignad **4** and metal ions were calculated from the collecting data. The evaluation process were performed on the SIRKO computer program [30]. The selected UV-VIS spectral data of titration system for ligand **4** complexes with Ni(II), Cu(II) and Zn(II) ions are shown in Tables 3.3, 3.4 and 3.5, respectively.

Table 3.3 (a) Selected UV-VIS spectrometric titration data of ligand **4**:Ni(II) system with metal to ligand ratio varied within 0.1 to 1, $C_{initial}$ of ligand and Ni(II) are 1.0×10^{-5} and 6.0×10^{-5} M, $V_{initial}$ is 3.00 cm^3

Volume (cm^3)	Wavelength (nm)																
	200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360
0.00	0.954	1.479	1.409	1.141	0.825	0.388	0.499	0.901	1.139	0.998	1.146	1.115	0.887	0.671	0.554	0.446	0.312
0.05	1.062	1.468	1.394	1.128	0.820	0.384	0.494	0.891	1.127	0.991	1.139	1.109	0.886	0.676	0.561	0.453	0.316
0.10	0.978	1.455	1.378	1.117	0.814	0.380	0.490	0.881	1.115	0.984	1.131	1.102	0.883	0.678	0.564	0.456	0.316
0.15	1.009	1.441	1.360	1.103	0.805	0.374	0.484	0.871	1.104	0.976	1.124	1.095	0.879	0.679	0.567	0.458	0.317
0.20	0.999	1.433	1.348	1.092	0.799	0.369	0.479	0.863	1.094	0.969	1.116	1.089	0.876	0.679	0.570	0.460	0.318
0.25	0.880	1.415	1.327	1.076	0.789	0.362	0.472	0.850	1.078	0.959	1.105	1.078	0.869	0.677	0.568	0.459	0.315
0.30	1.012	1.401	1.309	1.062	0.780	0.355	0.464	0.839	1.067	0.948	1.094	1.068	0.862	0.674	0.568	0.458	0.313
0.35	0.948	1.392	1.295	1.050	0.773	0.351	0.460	0.831	1.057	0.942	1.087	1.062	0.859	0.674	0.569	0.459	0.313
0.40	1.006	1.380	1.283	1.042	0.768	0.349	0.458	0.825	1.048	0.936	1.081	1.057	0.856	0.674	0.570	0.460	0.313
0.45	0.898	1.367	1.267	1.030	0.761	0.343	0.453	0.816	1.039	0.928	1.073	1.050	0.852	0.674	0.571	0.462	0.315
0.50	0.946	1.352	1.250	1.015	0.750	0.335	0.444	0.804	1.024	0.916	1.059	1.036	0.842	0.666	0.565	0.456	0.308
ε_L [a]	95.39	147.9	140.9	114.1	82.53	38.81	49.92	90.11	113.9	99.8	114.6	111.5	88.70	67.14	55.38	44.62	31.22

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

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 3.3 (b) Selected UV-VIS spectrometric titration data of ligand **4**:Ni(II) system with metal to ligand ratio varied within 1 to 11, $C_{initial}$ of ligand and Ni(II) are 1.0×10^{-5} and 6.0×10^{-4} M, $V_{initial}$ is 3.00 cm^3

Volume (cm^3)	Wavelength (nm)																
	200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360
0.00	1.025	1.505	1.413	1.150	0.822	0.390	0.513	0.926	1.162	0.992	1.124	1.097	0.874	0.656	0.533	0.427	0.300
0.05	0.955	1.492	1.391	1.133	0.816	0.380	0.503	0.909	1.145	0.988	1.123	1.096	0.879	0.670	0.551	0.441	0.306
0.10	1.023	1.479	1.372	1.117	0.810	0.373	0.495	0.895	1.130	0.981	1.118	1.092	0.880	0.679	0.563	0.451	0.310
0.15	0.978	1.472	1.357	1.107	0.807	0.371	0.492	0.887	1.122	0.979	1.117	1.092	0.883	0.687	0.573	0.460	0.315
0.20	0.922	1.459	1.340	1.094	0.801	0.367	0.487	0.875	1.109	0.972	1.109	1.085	0.880	0.690	0.578	0.465	0.316
0.25	1.016	1.448	1.322	1.081	0.795	0.364	0.484	0.866	1.097	0.965	1.101	1.077	0.877	0.691	0.581	0.467	0.316
0.30	0.854	1.441	1.308	1.070	0.789	0.360	0.480	0.857	1.086	0.958	1.093	1.070	0.871	0.689	0.580	0.466	0.313
0.35	0.903	1.433	1.294	1.061	0.785	0.360	0.480	0.852	1.078	0.953	1.087	1.065	0.870	0.692	0.585	0.471	0.318
0.40	0.954	1.415	1.275	1.046	0.777	0.358	0.477	0.844	1.068	0.947	1.080	1.060	0.868	0.694	0.589	0.476	0.322
0.45	0.922	1.412	1.264	1.039	0.774	0.358	0.477	0.838	1.061	0.941	1.072	1.050	0.862	0.691	0.587	0.474	0.320
0.50	0.929	1.401	1.253	1.031	0.771	0.359	0.478	0.834	1.054	0.936	1.066	1.046	0.860	0.692	0.589	0.477	0.324
0.55	0.888	1.389	1.238	1.019	0.762	0.354	0.472	0.824	1.042	0.927	1.056	1.036	0.853	0.687	0.587	0.475	0.322
ε_L [a]	10.25	15.05	14.13	11.50	8.22	3.90	5.13	9.26	11.62	9.92	11.24	10.97	8.74	6.56	5.33	4.27	3.00

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

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 3.4 (a) Selected UV-VIS spectrometric titration data of ligand **4:**Cu(II) system with metal to ligand ratio varied within 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

Titration volume (cm^3)	Wavelength (nm)										
	200	220	240	260	280	300	320	340	360	380	400
0.00	0.3018	0.5850	0.2397	0.2711	0.6262	0.2633	0.2274	0.0788	0.0168	0.0049	0.0015
0.05	0.3481	0.6073	0.2560	0.2795	0.6382	0.2664	0.2306	0.0807	0.0199	0.0083	0.0038
0.10	0.3633	0.5942	0.2865	0.3024	0.6398	0.2770	0.2299	0.0880	0.0350	0.0235	0.0158
0.15	0.3803	0.6122	0.2709	0.2986	0.6559	0.2716	0.2296	0.0811	0.0231	0.0113	0.0057
0.20	0.3718	0.6098	0.2736	0.2992	0.6543	0.2726	0.2302	0.0828	0.0256	0.0137	0.0075
0.25	0.3760	0.6088	0.2774	0.2999	0.6526	0.2741	0.2312	0.0844	0.0285	0.0171	0.0110
0.30	0.4285	0.6042	0.2807	0.3011	0.6500	0.2753	0.2310	0.0854	0.0299	0.0180	0.0113
0.35	0.3982	0.6008	0.2824	0.3013	0.6457	0.2753	0.2298	0.0852	0.0303	0.0186	0.0114
0.40	0.3576	0.5984	0.2834	0.3005	0.6417	0.2744	0.2287	0.0854	0.0316	0.0198	0.0126
0.45	0.3633	0.5942	0.2865	0.3024	0.6398	0.2770	0.2299	0.0880	0.0350	0.0235	0.0158
0.50	0.3699	0.5920	0.2890	0.3026	0.6358	0.2755	0.2278	0.0865	0.0343	0.0230	0.0148
ε_L[a]	30.18	58.5	23.97	27.11	62.62	26.33	22.74	7.88	1.68	0.49	0.15

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

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 3.4 (b) Selected UV-VIS spectrometric titration data of ligand **4:**Cu(II) system with metal to ligand ratio varied within 1 to 11, $C_{initial}$ of ligand and Cu(II) are 1.0×10^{-5} and 6.0×10^{-4} M, $V_{initial}$ is 3.00 cm^3

Titration volume (cm^3)	Wavelength (nm)										
	200	220	240	260	280	300	320	340	360	380	400
0.00	0.2900	0.5354	0.2106	0.1974	0.5457	0.2335	0.2208	0.0759	0.0154	0.0047	0.0015
0.05	0.3231	0.5799	0.2546	0.2231	0.5658	0.2545	0.2171	0.0798	0.0267	0.0151	0.0069
0.10	0.4247	0.5953	0.2830	0.2378	0.5705	0.2653	0.2113	0.0802	0.0331	0.0207	0.0092
0.15	0.3931	0.6100	0.3083	0.2528	0.5758	0.2804	0.2125	0.0858	0.0424	0.0294	0.0153
0.20	0.3987	0.6222	0.3307	0.2646	0.5768	0.2910	0.2105	0.0877	0.0478	0.0343	0.0181
0.25	0.4125	0.6356	0.3514	0.2749	0.5781	0.3008	0.2088	0.0895	0.0523	0.0384	0.0199
0.30	0.3994	0.6450	0.3682	0.2823	0.5769	0.3078	0.2056	0.0895	0.0549	0.0400	0.0195
0.35	0.3659	0.6551	0.3842	0.2893	0.5767	0.3157	0.2043	0.0917	0.0594	0.0446	0.0226
0.40	0.3369	0.6640	0.3986	0.2954	0.5765	0.3229	0.2027	0.0935	0.0636	0.0480	0.0248
0.45	0.3783	0.6766	0.4137	0.3026	0.5764	0.3291	0.2005	0.0933	0.0643	0.0481	0.0227
0.50	0.3761	0.6828	0.4234	0.3047	0.5724	0.3320	0.1968	0.0928	0.0660	0.0494	0.0231
ε_L [a]	29.00	53.54	21.06	19.74	54.57	23.35	22.08	7.59	1.54	0.47	0.15

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

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 3.5 (a) Selected UV-VIS spectrometric titration data of ligand **4**:Zn(II) system with metal to ligand ratio varied within 0.1 to 1, $C_{initial}$ of ligand and ZnII) are 1.0×10^{-5} and 6.0×10^{-5} M, $V_{initial}$ is 3.00 cm^3

Volume (cm^3)	Wavelength (nm)																
	200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360
0.00	1.212	1.514	1.459	1.179	0.907	0.455	0.536	0.902	1.136	1.073	1.260	1.220	0.980	0.775	0.672	0.559	0.400
0.05	1.110	1.544	1.476	1.192	0.907	0.464	0.536	0.902	1.144	1.073	1.257	1.220	0.973	0.767	0.672	0.551	0.396
0.10	1.135	1.537	1.464	1.180	0.907	0.456	0.536	0.902	1.134	1.073	1.245	1.220	0.965	0.762	0.672	0.547	0.393
0.15	0.997	1.523	1.449	1.169	0.907	0.451	0.536	0.902	1.124	1.073	1.234	1.220	0.959	0.759	0.672	0.546	0.391
0.20	0.992	1.511	1.435	1.158	0.907	0.444	0.536	0.902	1.113	1.073	1.222	1.220	0.951	0.755	0.672	0.542	0.388
0.25	0.981	1.499	1.423	1.148	0.907	0.440	0.536	0.902	1.107	1.073	1.214	1.220	0.947	0.753	0.672	0.542	0.387
0.30	1.077	1.489	1.414	1.141	0.907	0.436	0.536	0.902	1.099	1.073	1.203	1.220	0.941	0.749	0.672	0.538	0.382
0.35	1.062	1.476	1.398	1.132	0.907	0.436	0.536	0.902	1.093	1.073	1.198	1.220	0.940	0.752	0.672	0.543	0.387
0.40	0.904	1.460	1.375	1.114	0.907	0.427	0.536	0.902	1.077	1.073	1.179	1.220	0.928	0.744	0.672	0.537	0.382
0.45	1.080	1.452	1.366	1.108	0.907	0.424	0.536	0.902	1.073	1.073	1.171	1.220	0.923	0.741	0.672	0.534	0.379
0.50	0.937	1.435	1.349	1.095	0.907	0.417	0.536	0.902	1.061	1.073	1.159	1.220	0.915	0.736	0.672	0.530	0.376
ε_L[a]	121.2	151.4	145.9	117.9	90.7	45.5	53.6	90.2	113.6	107.3	126.0	122.0	98.0	77.5	67.2	55.9	40.0

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

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 3.5(b) Selected UV-VIS spectrometric titration data of ligand **4**:Zn(II) system with metal to ligand ratio varied within 1 to 11, $C_{initial}$ of ligand and ZnII) are 1.0×10^{-5} and 6.0×10^{-4} M, $V_{initial}$ is 3.00 cm^3

Volume (cm^3)	Wavelength (nm)																
	200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360
0.00	0.978	1.462	1.407	1.134	0.836	0.392	0.491	0.882	1.121	1.012	1.177	1.143	0.909	0.697	0.586	0.476	0.332
0.05	1.022	1.462	1.394	1.125	0.837	0.390	0.487	0.873	1.112	1.011	1.177	1.144	0.917	0.714	0.606	0.492	0.340
0.10	0.978	1.449	1.371	1.109	0.828	0.381	0.478	0.859	1.098	1.003	1.171	1.139	0.918	0.723	0.617	0.502	0.345
0.15	1.065	1.438	1.356	1.096	0.820	0.372	0.468	0.846	1.084	0.994	1.162	1.131	0.913	0.723	0.618	0.502	0.342
0.20	0.977	1.421	1.335	1.079	0.809	0.365	0.460	0.833	1.069	0.982	1.151	1.122	0.909	0.723	0.620	0.505	0.343
0.25	0.922	1.409	1.321	1.070	0.804	0.361	0.458	0.827	1.061	0.978	1.145	1.118	0.908	0.726	0.625	0.509	0.345
0.30	0.938	1.400	1.309	1.059	0.795	0.353	0.450	0.818	1.051	0.968	1.135	1.109	0.901	0.721	0.621	0.505	0.341
0.35	0.957	1.393	1.300	1.053	0.792	0.352	0.448	0.813	1.046	0.964	1.131	1.105	0.900	0.723	0.624	0.508	0.344
0.40	0.952	1.386	1.288	1.043	0.785	0.348	0.445	0.807	1.038	0.958	1.123	1.098	0.896	0.721	0.622	0.507	0.342
0.45	0.923	1.378	1.278	1.037	0.781	0.348	0.445	0.804	1.032	0.952	1.115	1.092	0.893	0.721	0.623	0.509	0.345
0.50	0.996	1.368	1.265	1.026	0.772	0.340	0.438	0.795	1.023	0.944	1.106	1.083	0.886	0.716	0.619	0.505	0.340
0.55	0.897	1.358	1.255	1.018	0.767	0.338	0.436	0.789	1.016	0.938	1.099	1.077	0.882	0.714	0.618	0.505	0.341
ε_L [a]	9.78	14.62	14.07	11.34	8.36	3.92	4.91	8.82	11.21	10.12	11.77	11.43	9.09	6.97	5.86	4.76	3.32

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

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

3.4 Quantum Chemical Calculations

3.4.1 Structure Optimization

The optimized structure of **1**, **2**, **3** and **4** were determined by semiempirical AM1 method. At first, the structure of **1**, **2**, **3** and **4** were build using standard geometrical parameters and optimized by AM1 method. Possible structures of all species of **1**, **2**, **3** and **4** including their deprotonated and protonated species were optimized. Optimized structures of zince complexes with **1**, **2**, **3** and **4** were also obtained.

3.4.2 Ab initio Calculations

The SCF energies of the optimized structures were determined by the *ab initio* calculations with 6-31G basis set. The all possible species of **1**, **2**, **3** and **4** were optimized and computed of their energies at the 6-31G and 6-31G* levels.

All calculations were performed on the Pentium II/350 IBM-PC300Gl of RAM 512 MB. The program Gaussian 94W [31] were used for all quantum-chemical computations. Countetpoise correction method was not included in all calculations.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Basicity Constant of 4 in aqueous solution

The chemical equilibria of **4** (symbolized as L) in potassium nitrate solution are written as following equations

$$K_1 : L^{2-} + H^+ \rightleftharpoons LH^- \quad (4.1)$$
$$K_2 : LH^- + H^+ \rightleftharpoons LH_2 \quad (4.2)$$
$$K_3 : LH_2 + H^+ \rightleftharpoons LH_3^+ \quad (4.3)$$
$$K_4 : LH_3^+ + H^+ \rightleftharpoons LH_4^{2+} \quad (4.4)$$

K_1, K_2, K_3, and K_4 are first, second, third and fourth protonation constants, so called basicity constants. The basicity constants of **4** in 0.5 M KNO_3, expressed in terms of logarithmic values are shown in Table 4.1.

Table 4.1 Logarithm of the basicity constant of **4** (**L**) in 0.5 M KNO_3 at various temperatures

Temperature (K)	log K_1	log K_2	log K_3	log K_4
293	10.64 ± 0.03	8.05 ± 0.08	5.88 ± 0.10	3.68 ± 0.18
298	10.48 ± 0.03	7.99 ± 0.08	4.71 ± 0.09	2.77 ± 0.19
303	10.41 ± 0.03	7.98 ± 0.08	4.45 ± 0.09	2.59 ± 0.21

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Gibb's free energy change of protonation reactions at 25 °C (298 K), ΔG^o were calculated from $- 686.634R \log K$ ($\Delta G^o = -2.303 RT \log K$). Due to a definition of Gibb's free energy ($\Delta G^o = \Delta H^o - T\Delta S^o$), then log K is $-\Delta H/2.303RT+\Delta S/2.303R$. Then the entyhalpy and entropy changes of protonation reactions were evaluated from slope and intercept of plot between log K against 1/T. The plot between log K and the reciprocal of the experimental temperatures in absolute unit is shown in Figure 4.1. The slope and intercept of these lines are -ΔH/2.303RT and +ΔS/2.303R, respectively. The estimate thermodynamics of protonation reaction at standard condition are shown in Table 4.2.

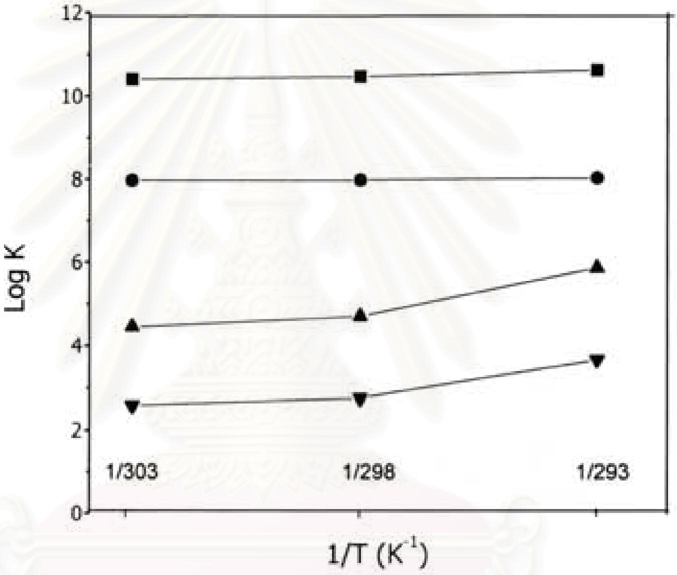


Figure 4.1 Plot between log K and 1/T for protonation reaction of the first (■■■), second (● ● ●), third (▲▲▲) and fourth (▼▼▼)

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.2 shows that reaction of the first and second protonation is an exothermic process. The entropy change of the first is much larger than the second reaction. Gibb's free energy changes of protonation reactions show their spontaneous reactions.

Table 4.2 Thermodynamics of protonation reaction at 298 K

Reaction	ΔH^{o} (kJ mol^{-1})	ΔG^{o} (kJ mol^{-1})	ΔS^{o} (JK^{-1}mol^{-1})
$L^{2-} + H^{+} \rightleftharpoons LH^{-}$	-20	-60	39
$LH^{-} + H^{+} \rightleftharpoons LH_2$	-33	-46	12
$LH_2 + H^{+} \rightleftharpoons LH_3^{+}$	[a]	-27	[a]
$LH_3^{+} + H^{+} \rightleftharpoons LH_4^{2+}$	[a]	-16	[a]

[a] not acceptable value due to non linearity of plot between log K and 1/T

The potentiometric titration curves of **4** (**L**) in 0.5 M KNO_3 are shown in Figure 4.1.

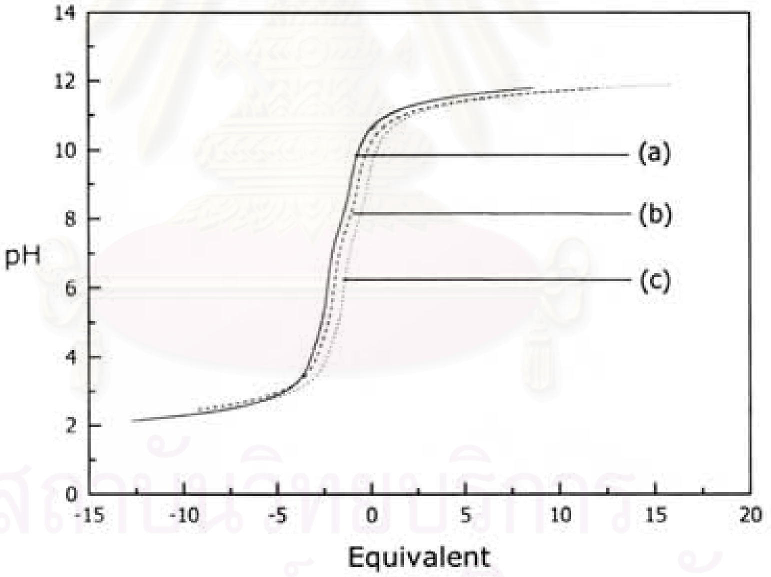


Figure 4.2 Potentiometric titration curves of **4** (**L**) in 0.5 M KNO_3 are shown at 25 °C, based on the initial concentration ratio of the ligand to proton (a) 1:8.5, (b) 1.8.8 and (c) 1:12; equivalent is defined as the ratio of ($n_{OH^-} - n_{acid}$) to n_{ligand}.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

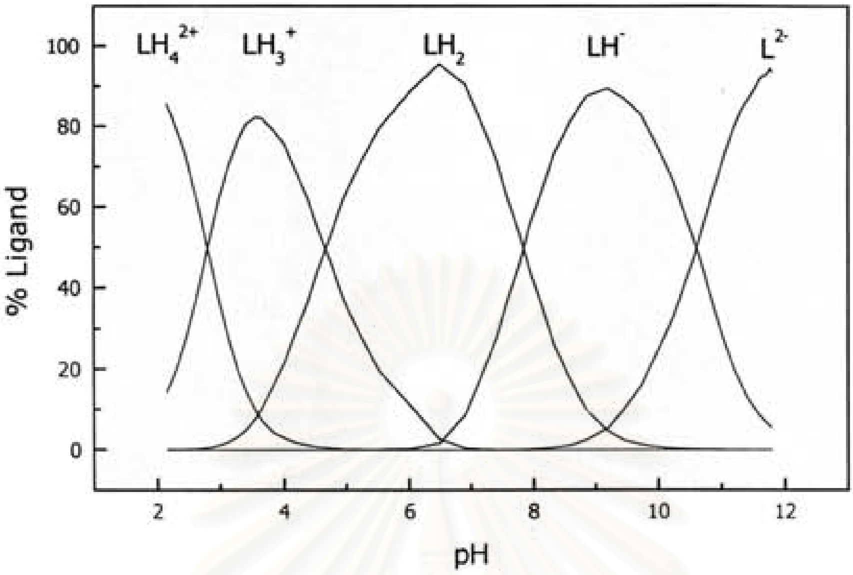


Figure 4.3 Distribution curves of **4 (L)** in 0.5 M KNO_3 at 25 °C

The basicity constants of **4** in 0.1 M KNO_3 at 25 °C, expressed in terms of logarithm are shown in Table 4.3.

Table 4.3 Logarithm of the basicity constant **4 (L)** in 0.1 M KNO_3 at 25 °C

	Reaction	log *K*
K_1 :	$L^{2-} + H^+ \rightleftharpoons LH^-$	10.06 ± 0.06
K_2 :	$LH^- + H^+ \rightleftharpoons LH_2$	7.96 ± 0.05
K_3 :	$LH_2 + H^+ \rightleftharpoons LH_3^+$	7.12 ± 0.10
K_4 :	$LH_3^+ + H^+ \rightleftharpoons LH_4^{2+}$	3.28 ± 0.10

The titration curves of **4 (L)** in 0.1 M KNO_3 are shown in Figure 4.3.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

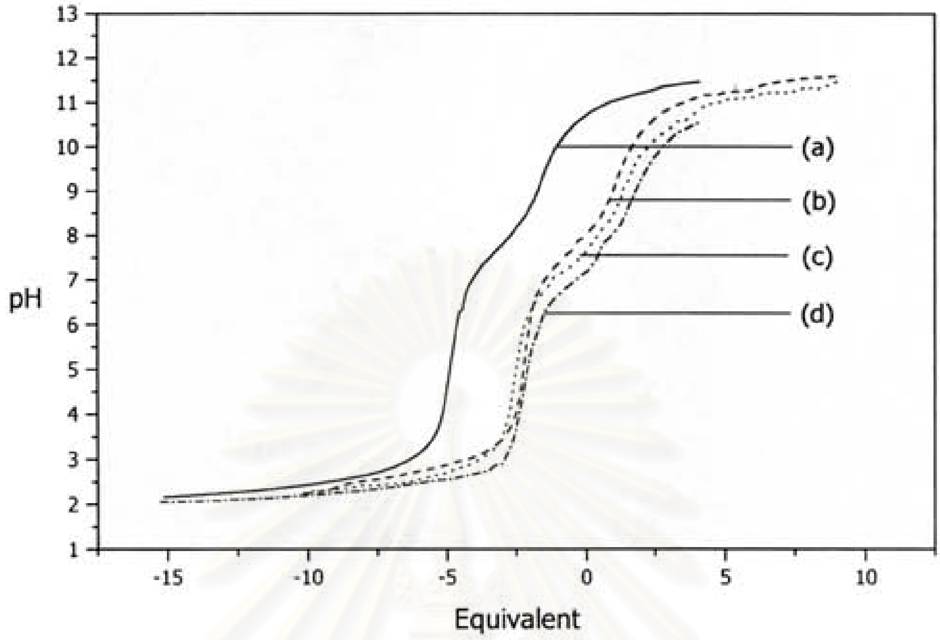


Figure 4.4 Potentiometric titration curves of **4 (L)** in 0.1 M KNO_3 are shown at 25 °C, based on the initial concentration ratio of the ligand to proton (a) 1:1.5, (b) 1:10, (c) 1:14 and (d) 1:15; equivalent is defined as the ratio of (n_{OH^-} - n_{acid}) to n_{ligand}.

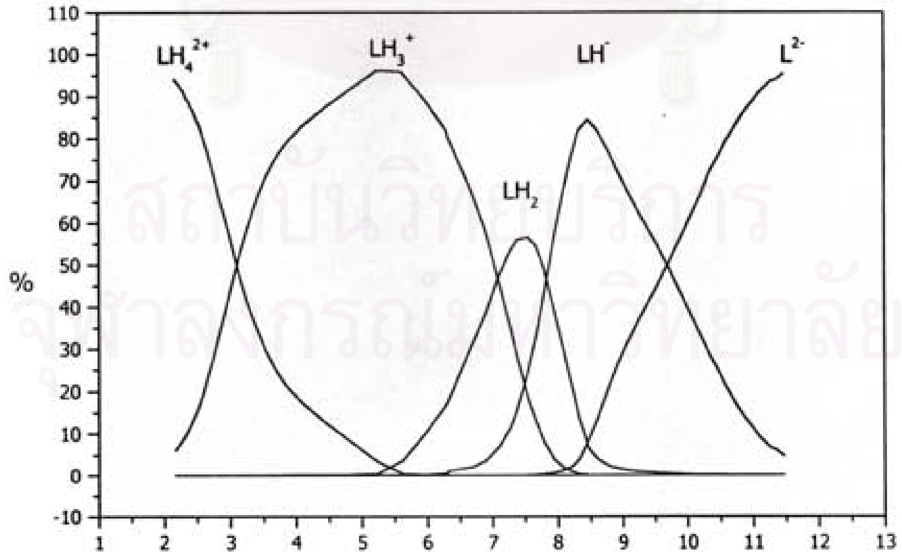


Figure 4.5 Distribution curves of **4 (L)** in 0.1 M KNO_3 at 25 °C

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

4.2 Complexation in aqueous solution by potentiometry

Potentiometric titration curves for systems of **4** and cobalt(II), nickel(II), copper (II) and zinc(II) are shown in Figures 4.5, 4.6, 4.7 and 4.8, respectively.

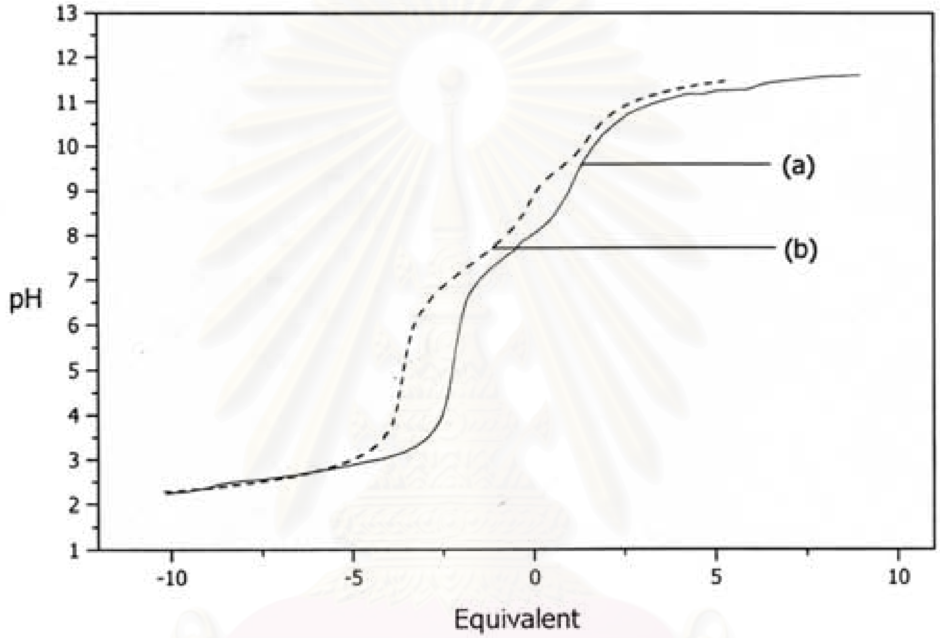


Figure 4.6 Typical titration curves for system of **4** and Co(II) at 25 °C in 0.1 M KNO_3 : (a) 1.0 mM **4**; (b) 1.0 mM **4** + 1.0 mM $Co(NO_3)_2$; equivalent is defined as the ratio of $(n_{OH^-} - n_{acid})$ to n_{ligand}.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

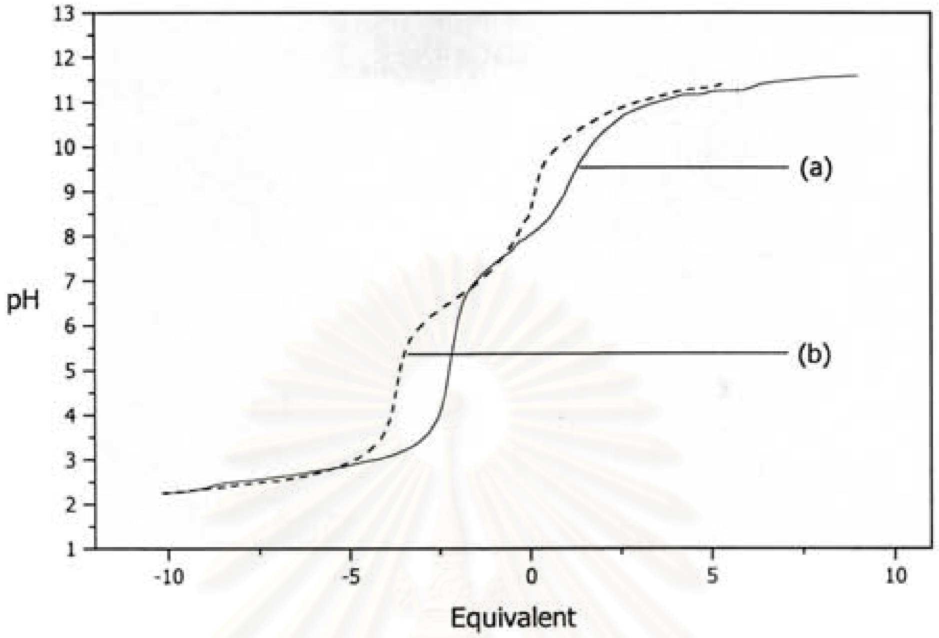


Figure 4.7 Typical titration curves for system of **4** and Ni(II) at 25 °C in 0.1 M KNO_3 : (a) 1.0 mM **4**; and (b) 1.0 mM **4** + 1.0 mM $Ni(NO_3)_2$; equivalent is defined as the ratio of $(n_{OH^-} - n_{acid})$ to n_{ligand}.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

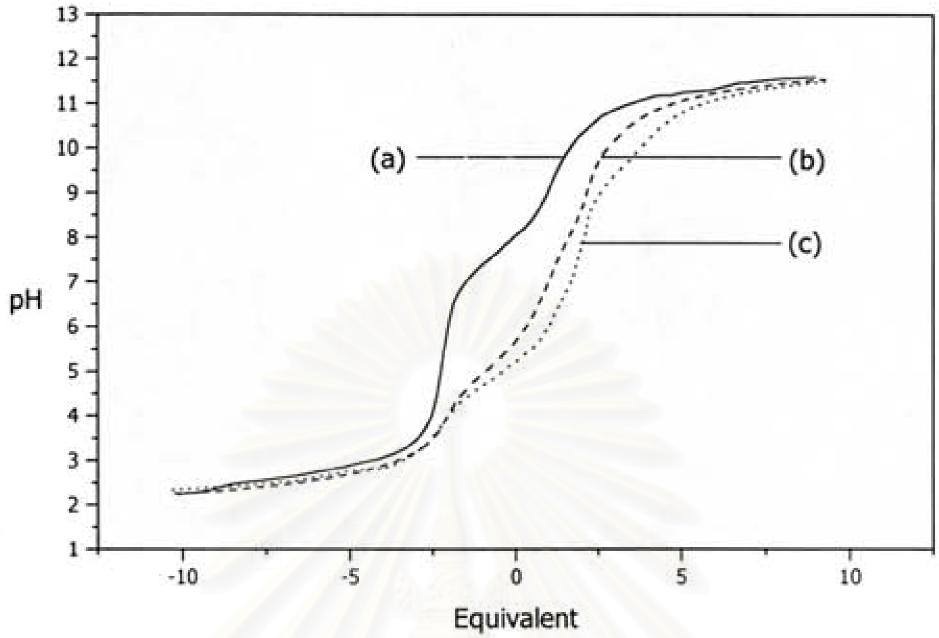


Figure 4.8 Typical titration curves for system of **4** and Cu(II) at 25 °C in 0.1 M KNO_3 : (a) 1.0 mM **4**; (b) 1.0 mM **4** + 1.0 mM $Cu(NO_3)_2$ and (c) 1.0 mM **4** + 1.5 mM $Cu(NO_3)_2$; equivalent is defined as the ratio of (n_{OH^-} - n_{acid}) to n_{ligand}.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

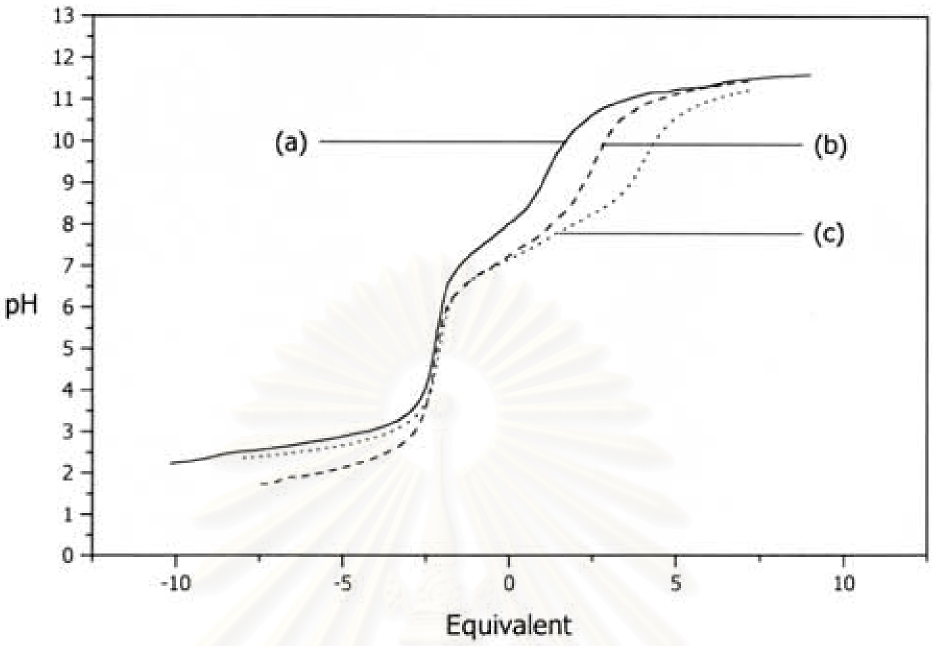


Figure 4.9 Typical titration curves for **4** and Zn(II) at 25 °C in 0.1 M KNO_3 : (a) 1.0 mM **4**; (b) 1.0 mM **4** + 1.0 mM $Zn(NO_3)_2$ and (c) 1.0 mM **4** + 1.5 mM $Zn(NO_3)_2$; equivalent is defined as the ratio of $(n_{OH^-} - n_{acid})$ to n_{ligand}.

Evaluation for stability constants of **4**/Co(II), **4**/Ni(II), **4**/Cu(II) and **4**/Zn(II) complexes in water, in 0.1 M KNO_3 can not be obtained. Complexation of these complexes should be formed. A reason of unsuccessful evaluations for these complexes is that complexes between these metal ions and hydroxide ions in water are formed and become dominant species in aqueous solution. The soluble hydoxide complexes for these metal ions must be $[Co(OH)]^+$, $[Ni(OH)]^+$, $[Cu(OH)]^+$ and $[Zn(OH)]^+$ and precipitated complexes should be $Co(OH)_2$, $Ni(OH)_2$, $Cu(OH)_2$, $Zn(OH)_2$, respectively. To avoid the formations of hydroxide complexes is to investigate complex formation of **4**/Co(II), **4**/Ni(II), **4**/Cu(II) and **4**/Zn(II) complexes in methanol.

The complex formation of Co(II), Ni(II), Cu(II), Zn(II) and **4** in methanol can be investigated by potentiometric and UV-VIS spectrometric titations. The quick method for determination of stability constants at certain pH is the UV-VIS spectrometry.

4.3 Complexation in methanol by UV-VIS Spectrometry

Uv spectrometric data obtained from uv titration of **4**/Ni(II) system (Table 3.3), **4**/Cu(II) system (Table 3.4) and **4**/Zn(II) system (Table 3.5) are shown in Figures 4.10 and 4.11, Figures 4.12 and 4.13, Figures 4.14 and 4.15, respectively.

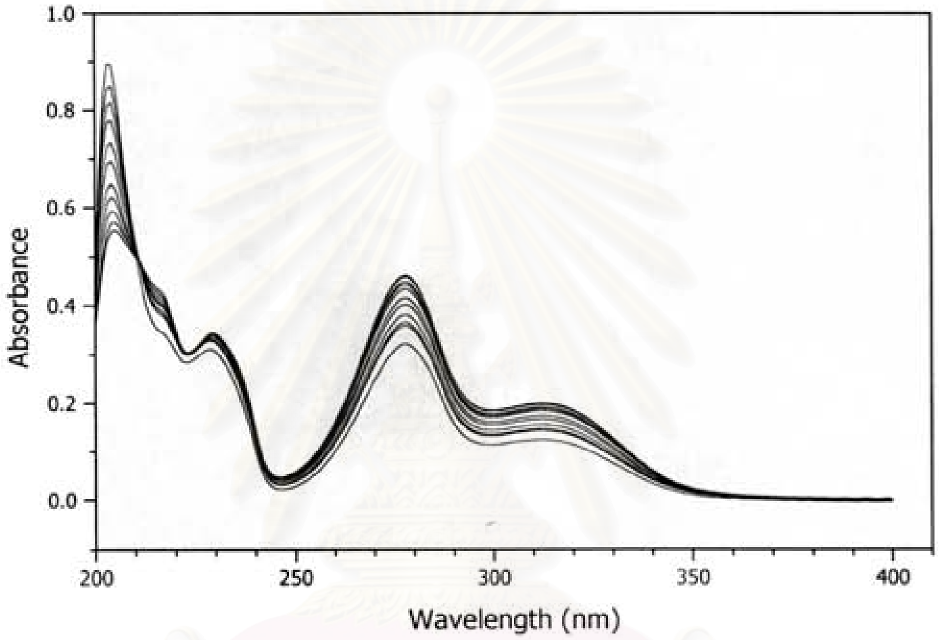


Figure 4.10 UV spectra obtained from uv spectrometric titration for **4**/Ni(II) system which Ni(II):**4** ratio varied within 0.1 to 1.

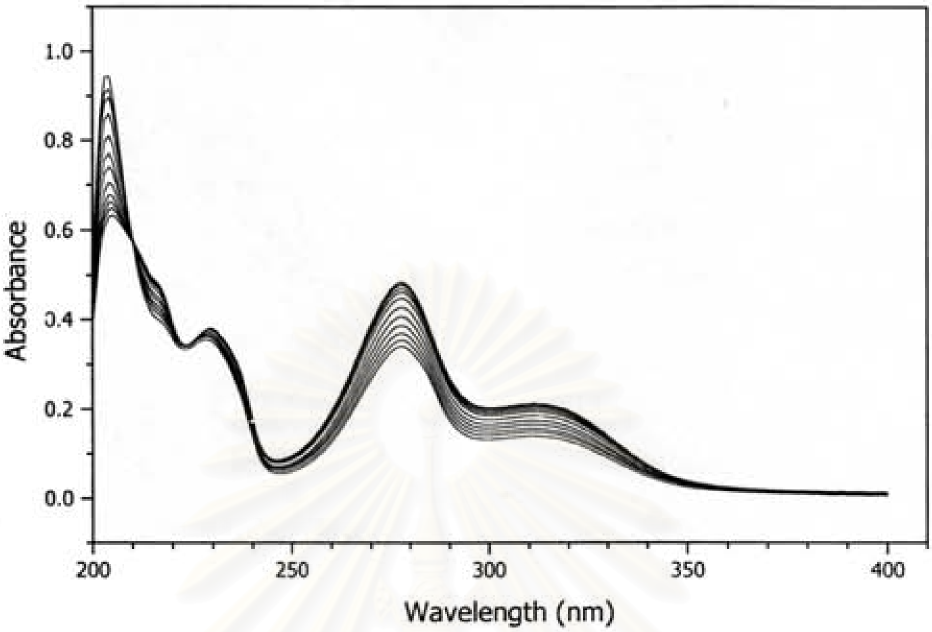


Figure 4.11 UV spectra obtained from uv spectrometric titration for **4**/Ni(II) system which Ni(II):**4** ratio varied within 1 to 11.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

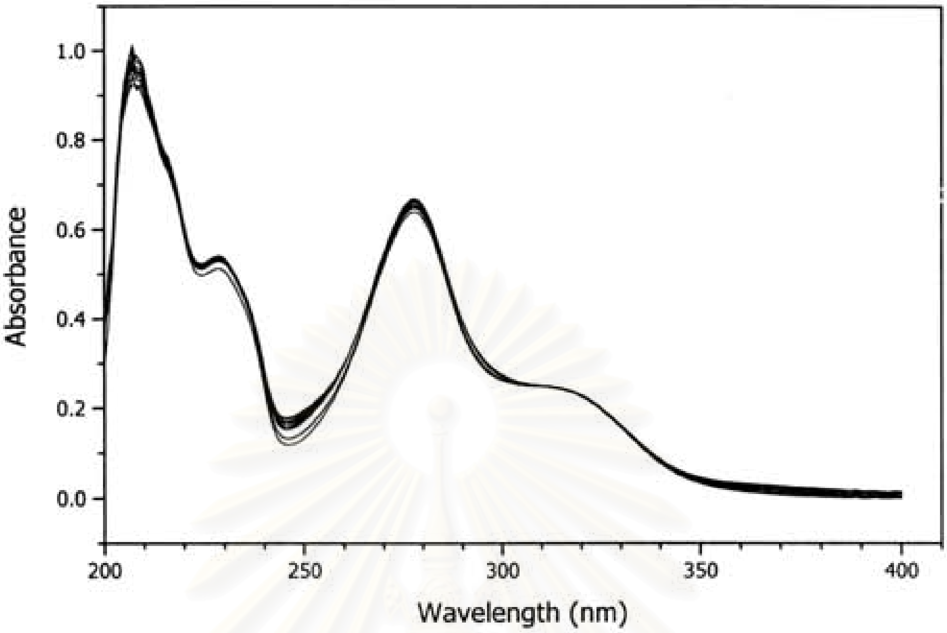


Figure 4.12 UV spectra obtained from uv spectrometric titration for **4**/Cu(II) system which Cu(II):**4** ratio varied within 0.1 to 1.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

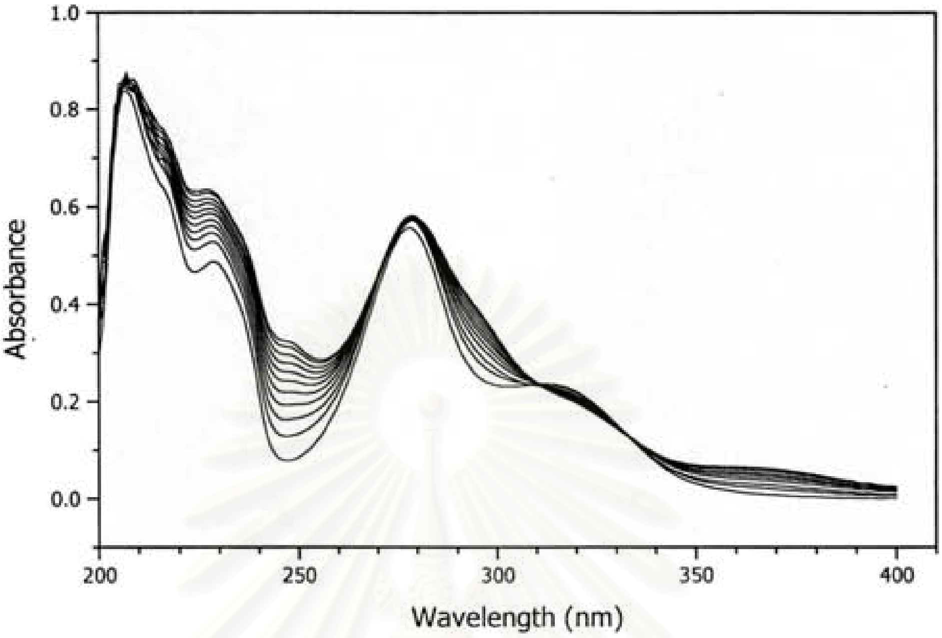


Figure 4.13 UV spectra obtained from uv spectrometric titration for **4**/Cu(II) system which Cu(II):**4** ratio varied within 1 to 11.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

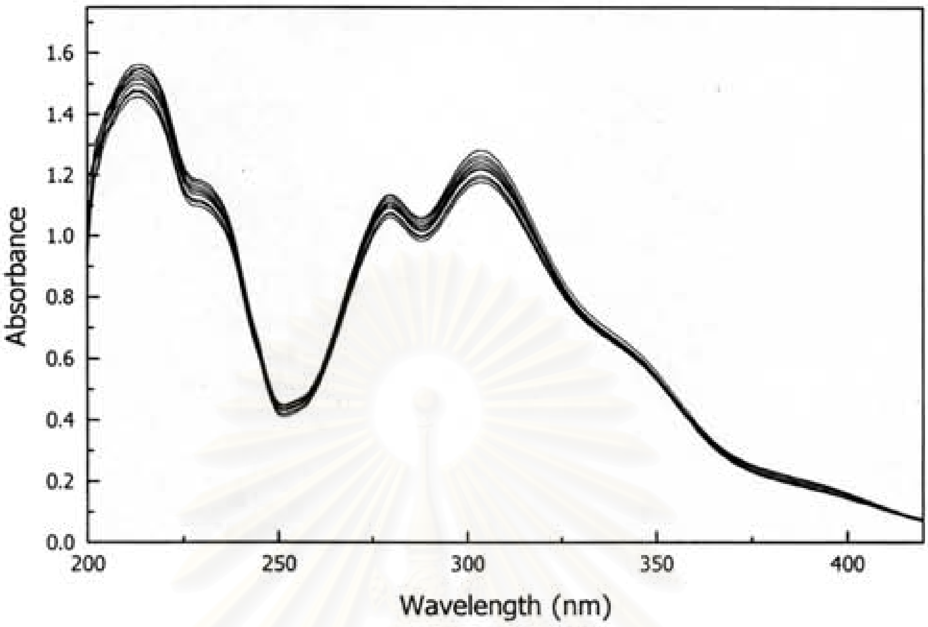


Figure 4.14 UV spectra obtained from uv spectrometric titration for **4**/Zn(II) system which Zn(II):**4** ratio varied within 0.1 to 1.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

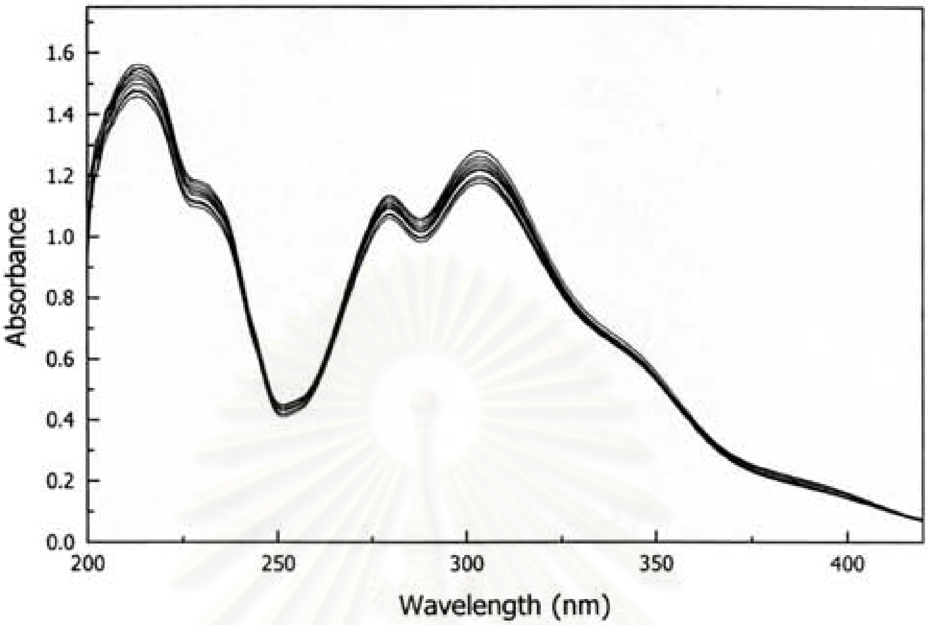


Figure 4.15 UV spectra obtained from uv spectrometric titration for **4**/Zn(II) system which Zn(II):**4** ratio varied within 1 to 11.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

The stability constants of **4** complexes with Ni(II), Cu(II) and Zn(II) in 0.01 M $Bu_4NCF_3SO_3$ in methanol expressed in terms of logarithm are shown in Table 4.4.

Table 4.4 Logarithm of stability constants of **4** complexes with Ni(II), Cu(II) and Zn(II) at rooom temperature.

4/M(II) Complex	log β_1 [a]	log β_1 [b]	log β_1 [c]
Ni(II)	4.31 ± 0.006	3.28 ± 0.004	3.80 ± 0.01
Cu(II)	4.53 ± 0.004	4.02 ± 0.002	4.28 ± 0.01
Zn(II)	4.38 ± 0.006	4.35 ± 0.008	4.37 ± 0.01

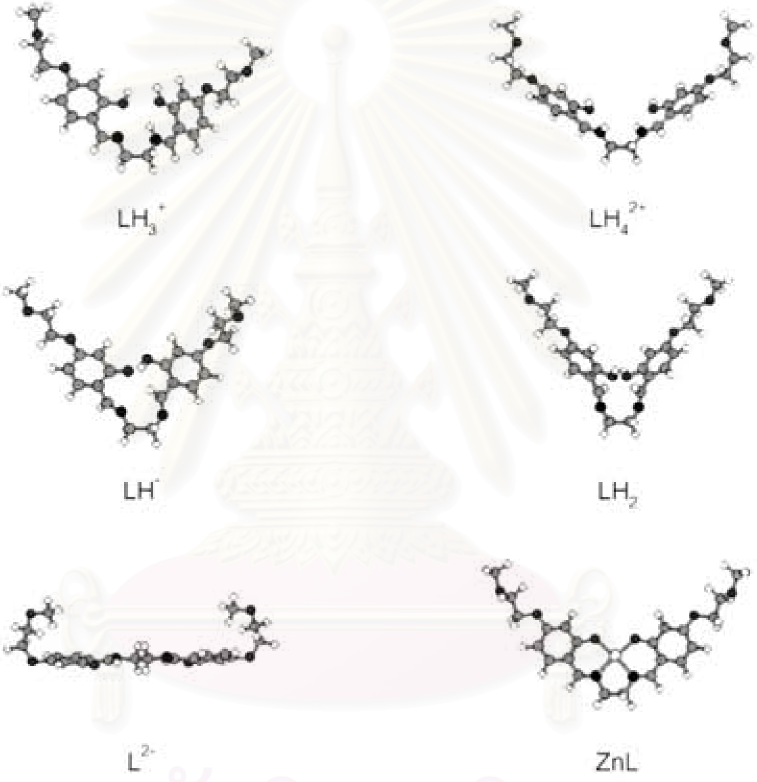
[a] at metal:ligand within 0.1 to 1, [b] at metal:ligand within 1 to 11, [c] average values,

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

4.4 Quantum chemical calculations

4.4.1 Structure optimization

Structures of **1**, **2**, **3**, **4**, their protonated and deprotonated species and their zinc complexes obtained from the AM1-optimizations are shown in Figure 4.16, 4.17, 4.18 and 4.19.

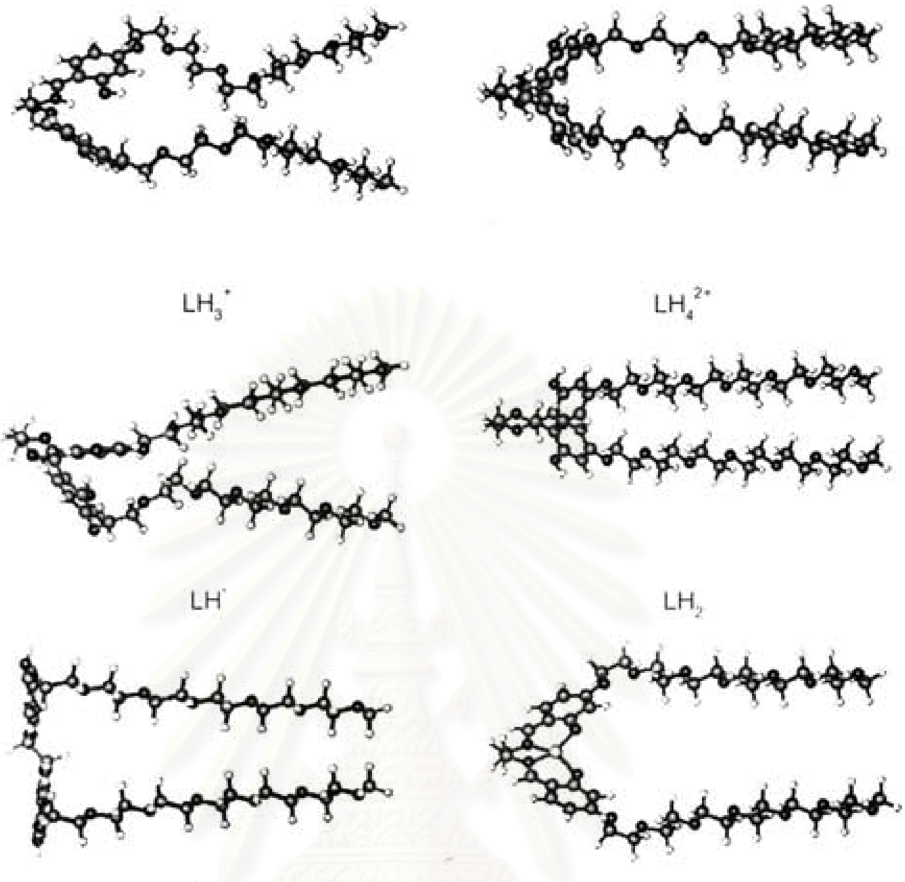


หอสมุดกลาง สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Figure 4.16 The optimized structure of **1** and their protonated, deprotonated species and zinc complex determined by AM1 method of quantum-chemical calculations

The L^{2-}, LH_2, LH_4^{2+} species and ZnL complex for ligand **1** (see Figure 4.16) are in C_2 symmetry group but for ligand **2** (see Figure 4.17), only LH_2, LH_4^{2+} and ZnL complex species are in C_2 symmetry group. The L^{2-}, LH_2, LH_4^{2+} species for ligand **3** and **4** (see Figure 4.18 and 4.19) are in C_2 symmetry group.



LH_3^+ LH_4^{2+}

LH^- LH_2

L^{2-} ZnL

Figure 4.17 The optimized structure of **2** and their protonated, deprotonated species and zinc complex determined by AM1 method of quantum-chemical calculations

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

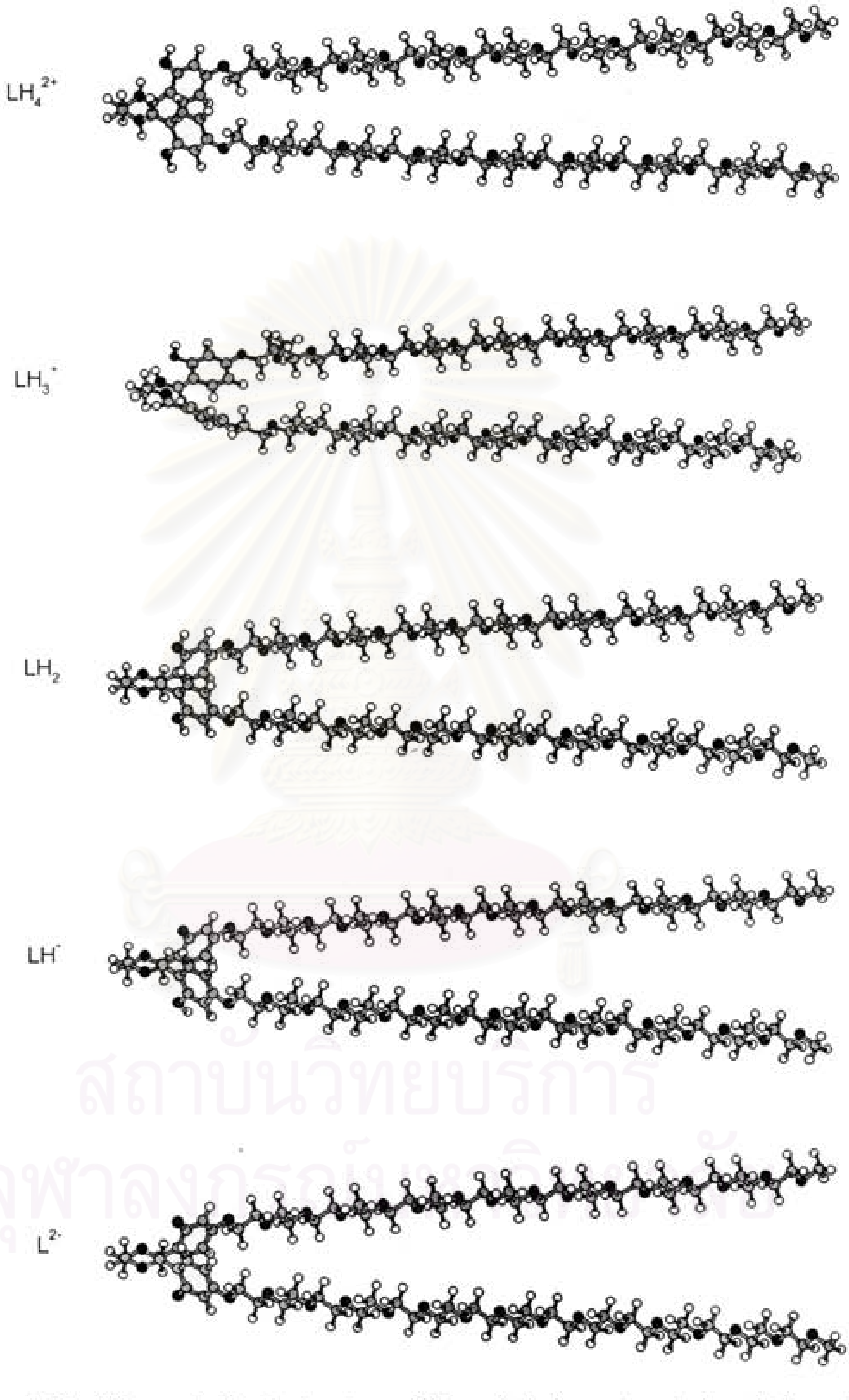


Figure 4.18 The optimized structure of **3** and their protonated and deprotonated species determined by AM1 method of quantum-chemical calculations

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

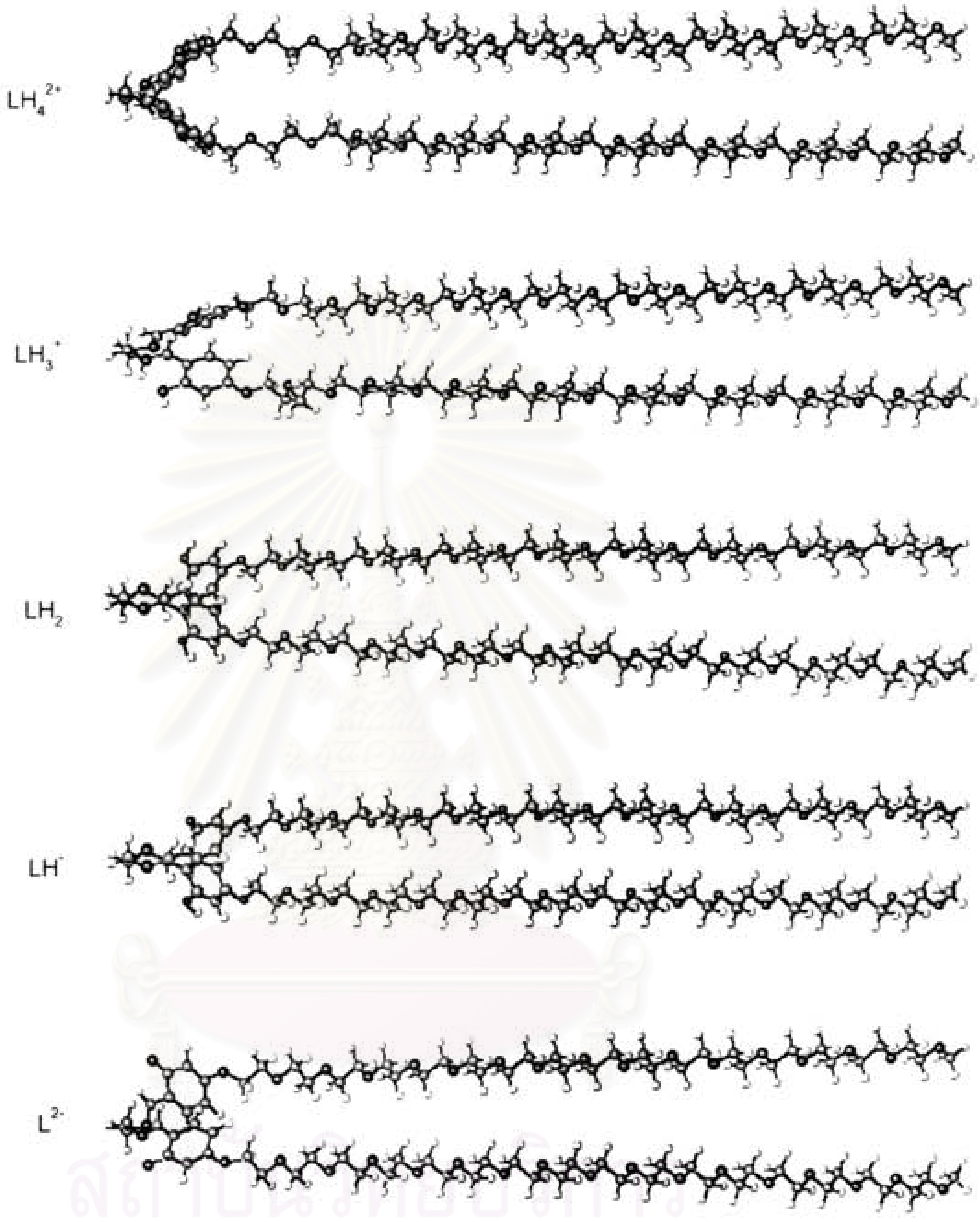


Figure 4.19 The optimized structure of **4** and their protonated and deprotonated species determined by AM1 method of quantum-chemical calculations

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

4.4.2 Energy Calculations

Total energies of the optimized structures of ligand **1** calculated by ab initio method with 6-31G and 6-31G* levels are shown in Table 4.5. Related energies of **1** and stabilization energies of its complex formation are shown in Table 4.6.

Table 4.5 Total energy at 6-31G and 6-31G* levels, dipole moment (μ) and atomic charge (q)of nitrogen of all species of **1**

Species	Total energy [a]		μ [b]
	6-31G	6-31G*	
L^{2-}	-1405.542692	-1406.139835	6.867
LH^-	-1406.187491	-1406.786315	5.902
LH_2	-1406.724480	-1407.324265	5.555
$L\,H_3^+$	-1407.167385	-1407.759782	10.472
$L\,H_4^{2+}$	-1407.502772	-1408.084906	12.548
$L[Zn]^{2-}$	-1405.416092	-	-
Zn^{2+}	-1776.612074	-1776.612074	0.0
ZnL	-3183.217782	-	5.940

[a] in hartree, [b] in debye at 6-31G* level

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.6 Total energy of all species of **1**, their related energies and stabilization energies of complex formation.

Species	Total energy [a]	Related energy [b, c]	ΔE [c]
L^{2-}	-1405.542692	1230.0	-
LH^{-}	-1406.187491	825.4	-404.6
LH_2	-1406.724480	488.4	-337.0
$L\ H_3^{+}$	-1407.167385	210.5	-277.9
$L\ H_4^{2+}$	-1407.502772	0	-210.5
$L[\mathit{Zn}]^{2-}$	-1405.416092 [d]	-	-
Zn^{2+}	-1776.612074	-	-
ZnL	-3183.217782	-	-746.5 [e], -667.1

[a] in hartree at 6-31G* level, [b] in kcal mol^{-1} relative to most stable species,
[c] binding energies in kcal mol^{-1}, [d] in hartree at 6-31G level,
[e] counter poise corrected value

Total energies of the optimized structures of ligand **2** calculated by ab initio method with 6-31G and 6-31G* levels are shown in Table 4.7. Related energies of **2** and stabilization energies of its complex formation are shown in Table 4.8.

Table 4.7 Total energy at 6-31G and 6-31G* levels, dipole moment (μ) and atomic charge (q) of nitrogen of all species of **2**

Species	Total energy [a]		μ [b]
	6-31G	6-31G*	
L^{2-}	-2934.005927	-2935.293391	64.160
LH^{-}	-2934.595344	-2935.879667	29.645
LH_2	-2935.138383	-2936.423566	4.412
$L\ H_3^{+}$	-2935.568473	-2936.846699	35.012
$L\ H_4^{2+}$	-2935.903182	-2937.171467	68.086
Zn^{2+}	-1776.612074	-1776.612074	0.0
ZnL	-	-4712.874781	7.547

[a] in hartree, [b] in debye at 6-31G* level

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.8 Total energy of all species of **2**, their related energies and stabilization energies of complex formation.

Species	Total energy [a]	Related energy [b]	ΔE [c]
L^{2-}	-2935.293391	1178.5	-
LH^-	-2935.879667	810.6	-367.9
LH_2	-2936.423566	469.3	-341.3
$L\ H_3^+$	-2936.846699	203.8	-265.5
$L\ H_4^{2+}$	-2937.171467	0.0	-203.8
Zn^{2+}	-1776.612074	-	
ZnL	-4712.874781	-	-608.3

[a] in hartree at 6-31G* level, [b] in kcal mol^{-1} relative to most stable species,
[c] binding energies in kcal mol^{-1}

The deprotonation and complexation processes for ligand **1** and **2** are shown in terms of the stabilization energies as following scheme:

Ligand **1** :

$$\begin{tikzcd}
L^{2-} \arrow[r, phantom, "\xrightleftharpoons{-H^+}"] \arrow[d, shift left] & LH^- \arrow[r, phantom, "\xrightleftharpoons{-H^+}"] & LH_2 \\
L^{2-}\mathit{preorg.} \arrow[u, shift left] \arrow[r, phantom, "\xrightleftharpoons{+\ Zn^{2+}}"] & LZn & \Delta E_{complex} = -667.1\ \mathrm{kcal\ mol^{-1}}
\end{tikzcd}$$

Ligand **2** :

$$\begin{tikzcd}
L^{2-} \arrow[r, phantom, "\xrightleftharpoons{-H^+}"] \arrow[d, shift left] & LH^- \arrow[r, phantom, "\xrightleftharpoons{-H^+}"] & LH_2 \\
L^{2-}\mathit{preorg.} \arrow[u, shift left] \arrow[r, phantom, "\xrightleftharpoons{+\ Zn^{2+}}"] & LZn & \Delta E_{complex} = -608.3\ \mathrm{kcal\ mol^{-1}}
\end{tikzcd}$$

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Total energies of the optimized structures of ligand **3** calculated by *ab initio* method with 6-31G levels are shown in Table 4.9. Related energies of **3** and stabilization energies of its complex formation are shown in Table 4.10.

Table 4.9 Total energy at 6-31G level, dipole moment (μ) and atomic charge (q)of nitrogen of all species of **3**

Species	Total energy [a]	μ [b]
	6-31G	
L^{2-}	-5685.084939	180.25
LH^-	-5685.700010	93.610
LH_2	-5686.283680	5.793
$L\,H_3^+$	-5686.725838	87.875
$L\,H_4^{2+}$	-5687.062808	179.80

[a] in hartree, [b] in debye

Table 4.10 Total energy of all species of **3**, their related energies and stabilization energies of complex formation.

Species	Total energy [a]	Related energy [b]	ΔE [c]
L^{2-}	-5685.084939	1241.1	-
LH^-	-5685.700010	855.2	-386.0
LH_2	-5686.283680	488.9	-366.2
$L\,H_3^+$	-5686.725838	211.4	-277.4
$L\,H_4^{2+}$	-5687.062808	0	-211.4

[a] in hartree at 6-31G level, [b] in kcal mol^{-1} relative to most stable species,
[c] binding energies in kcal mol^{-1}

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.11 Total energy at 6-31G level, dipole moment (μ) and atomic charge (q) of nitrogen of all species of **4**

Species	Total energy [a]	μ [b]
	6-31G	
L^{2-}	-5993.422148	199.69
LH^{-}	-5994.051938	97.71
LH_2	-5994.621991	4.68
$L\ H_3^{+}$	-5995.054335	94.76
$L\ H_4^{2+}$	-5995.365868	187.21

[a] in hartree 6-31G level, [b] in debye

Table 4.12 Total energy of all species of **4**, their related energies and stabilization energies of complex formation.

Species	Total energy [a]	Related energy [b]	ΔE [c]
L^{2-}	-5993.422148	1219.8	-
LH^{-}	-5994.051938	824.6	-395.2
LH_2	-5994.621991	466.8	-357.7
$L\ H_3^{+}$	-5995.054335	195.5	-271.3
$L\ H_4^{2+}$	-5995.365868	0.0	-195.5

[a] in hartree, [b] in kcal mol^{-1} relative to most stable species,
[c] binding energies in kcal mol^{-1}

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.13 Total energy, stabilization energy of protonation (ΔE) of **4** and related species computed by HF/6-31G and protonation constants of **4** in 0.5 M KNO_3 at 298 K.

species	Total energy (hartree)	ΔE (kcal mol^{-1})	Log *K*
L^{2-}	-5993.422148	-	-
LH^-	-5994.051938	-395.2	10.48 ± 0.03
LH_2	-5994.621991	-357.7	7.97 ± 0.08
$L H_3^+$	-5995.054335	-271.3	4.71 ± 0.09
$L H_4^{2+}$	-5995.365868	-195.5	2.77 ± 0.19

Table 4.14 Comparison of stabilization energies of protonations of **1**, **2**, **3** and **4**

Reaction	**1**	**2**	**3**	**4**
1st protonation	-404.6	-367.9	-386.0	-395.2
2nd protonation	-337.0	-341.3	-366.2	-357.7
3rd protonation	-277.9	-265.5	-277.4	-271.3
4th protonation	-210.5	-203.8	-211.4	-195.5
Complexation	-667.1	-608.3	-	-

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

หอสมุดกลาง สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER V

CONCLUSION

This research work can be concluded as following. Salen derivative **4** was synthesized and studied for determination of its protonation constants by potentiometric titration. The protonation constants at 25 °C in 0.1 and 0.5 M KNO_3 are log K_1=10.06, log K_2=7.96, log K_3=7.12, log K_4=3.28 and log K_1=10.48, log K_2=7.99, log K_3=4.71, log K_4=2.77, respectively. The evaluated enthalpy, Gibb's energy and entropy changes for protonation reactions at 298 K are :

Reaction	ΔH^o (kJ mol^{-1})	ΔG^o (kJ mol^{-1})	ΔS^o ($JK^{-1}mol^{-1}$)
$L^{2-} + H^+ \rightleftharpoons LH^-$	-20	-60	39
$LH^- + H^+ \rightleftharpoons LH_2$	-33	-46	12
$LH_2 + H^+ \rightleftharpoons LH_3^+$	not acceptable	-27	not acceptable
$LH_3^+ + H^+ \rightleftharpoons LH_4^{2+}$	not acceptable	-16	not acceptable

Complexation in aqueous solution of **4** and Ni(II), Cu(II) and Zn(II) were detected but their values could not be evaluated. Stability constants for ligand **4** complexes with Ni(II), Cu(II) and Zn(II) in 0.01 M $Bu_4NCF_3SO_3$ in MeOH were determined by UV-VIS spectrometric titration. The complexation constants, log β_{11}, of complexes between ligan **4** and Ni(II), Cu(II) and Zin(II) are 3.80, 4.28 and 4.37, respectively.

Optimized structures of ligands **1**, **2**, **3** and **4** and their related species were obatined by AM1 semi-empirical method. Stabilization energies for protonations of L^{2-} form of **1**, **2**, **3** and **4** calculated by *ab initio* method at 6-31G level and complexation energies of Zn(II) complexes with ligands **1** and **2** are :

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Reaction	Ligand			
	1	**2**	**3**	**4**
1st protonation	-404.6	-367.9	-386.0	-395.2
2nd protonation	-337.0	-341.3	-366.2	-357.7
3rd protonation	-277.9	-265.5	-277.4	-271.3
4th protonation	-210.5	-203.8	-211.4	-195.5
Complexation	-667.1	-608.3	not determine	not determine

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

REFERENCES

1. Adam W.; Roschmann K.J.; Saha-Moller C.R. *European J. Org.Chem.*, **2000**, *21*, 3519.
2. Bansal V.; Sharma P.K.; Banerji K.K. *Indian J. Chem. Inorg. Bio Inorg. Phys. Theo. Anal.Chem.*, **2000**, *39: (6)*, 654.
3.
4. Nishida T.; Miyafuji A.; Ito Y.N.; Katsuki T. *Tetrahedron Letters*, **2000**, *41: (36)*, 7053.
5. Sabater, M. J.; Alvaro, M.; Garcia, H.; Palomares, E.; Scaiano, J. C. *J. Am. Chem. Soc.*, **2001**: *123(29)*,7074.
6. Haus A.; Raidt M.; Link T.A.; Elias H. *Inorg. Chem.*, **2000**, *39: (22)*, 5111.
7. Agustin D.; Rima G.; Gornitzka H.; Barrau J. *Organometallics*, **2000**,*19:(21)*, 4276.
8. Shinoura X., Kita S., Ohba M., Okawa H., Furutachi H., Suzuki M., *Inorg. Chem.*, **2000**, *39:(20)*, 4520.
9. Pasini A., Demartin F., Piovesana O., Chiari B., Cinti A., Crispu O. *J. Chem. Soc. Dalton Trans.*, **2000**, 3467.
10. Belokon Y.N., Davies R.G., North M. *Tetrahedron Letters*, **2000**, *41: (37)* 7245.
11. Garcia M.I.F., Fondo M., Deibe A.M.G., Fernandez M.B.F., Gonzalez A.M., *Zeit. Anorg. Allg. Chem.*, **2000**, *626:(9)*, 1985.
12. Ikeda R., Tanaka H., Uyama H., Kobayashi S. *Macromolecules*, **2000**, *33:(18)*, 6648.
13. Hartley, F.R.; Hurgess, C.; Alcock, R.M. *Solution Equilibria*. England: Ellis Horwood Ltd., **1980**.
14. Gans, P.; Sabatini, A.; Vacca, A. *J. Chem. Soc. Dalton Trans.*, **1985**.1195.
15. Hehre, W.J.; Steward, R.F.; Pople, J.A. *J. Chem. Phys.*, **1969**, *51*, 2657.
16. Binkley, J.S.; Pople, J.A.; Hehre W.J. *J. Am. Chem. Soc.*, **1980**, *102*, 939.
17. Gordon, M.S., Binkley, J.S., Pople, J.A., Pietro, W.J. and Hehre W.J. *J. Am. Chem. Soc.*, **1982**, *104*, 2797.
18. Pietro, W.J.; Francl, M.M.; Hehre W.J.; Defrees, D.J.; Pople, J.A.; Binkley, J.S. *J. Am. Chem. Soc.*, **1982**, *104*, 5039.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

19. Dobbs K.D.; Hehre, W.J. *J.Com. Chem.*, **1986**, *7*, 359.

20. Dobbs K.D.; Hehre, W.J. *J.Com. Chem.*, **1987**, *8*, 861.

21. Dobbs K.D.; Hehre, W.J. *J.Com. Chem.*, **1987**, *8*, 880.

22. Ditchfield, R., Hehre, W.J. and Pople, J.A. *J. Chem. Phys.*, **1971**, *54*, 724.

23. Hehre, W.J., Ditchfield, R. and Pople, J.A. *J. Chem. Phys.*, **1972**, *56*, 2257.

24. Harihanran P.C. and Pople, J.A. *Mol Phys.*, **1974**, *27*, 209.

25. Gordon, M.S. *Chem. Phys. Lett.*, **1980**, *76*, 163.

26. Harihanran P.C. and Pople, J.A. *Theo. Chim. Acta.*, **1973**, *28*, 213.

27. Dunning, T.H. and Hay, P.J., *In Modern Theoretical Chemistry*, Ed. Schafer, H.F. III, Plenum, New York, **1976**.

28. McLean, A.D. and Chandler, G.S. *J. Chem. Phys.*, **1980**, *72*, 5639.

29. Boys, S.F.; Bernardi J. *Mol. Phys.* **1970**, *19*, 553.

30. Steward, J.J.P. *Rev. Comput. Chem.* **1990**, *1*, 45.

31. Vetrogon, V; Lukyanenko, N.G.; Schwing-Weill, M.J.; Arnaud-Neu, F. *Talanta* **1994**, *41*, 2105.

32. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defress, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94W, Revision D.1; Gaussian Inc., Pittsburgh, PA, **1995**.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย