

**SYNTHESIS AND CHARACTERIZATION OF GALLIUM (III) COMPLEXES
WITH CHALCONE AND SCHIFF BASE LIGANDS**

P.KHIDMAT MAKLUMAT AKADEMIK
UNIMAS



1000128288


CHIAU SHIS HOONG

This project is submitted in partial fulfillment of
the requirements for the degree of Bachelor of Science with Honours
(Resource Chemistry)

Faculty of Resource Science and Technology
UNIVERSITI MALAYSIA SARAWAK
2004

DECLARATION

No portion of the work referred to in this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.



Chiau Shis Hoong
Program of Resource Chemistry
Faculty of Resource Science and Technology
University Malaysia Sarawak

ACKNOWLEDGEMENTS

Gratefully acknowledgements are due to my project supervisor, Mr. Tay Meng Guan for his tutelage, forbearance and generosity to assist me in various aspects until the final chapter of my project. I extend my appreciation to Associate Prof. Dr Yeap Guan Yeow and Mr. Aw Yeong, School of Chemical Sciences, USM who helped in obtaining the CHN and ^1H NMR spectra and Dr. Md. Abu Affan kindly shepherded me to finish my project.

My totally inadequate thanks are also due to all the technical staff and lab assistants for their proficient assistance and providing the necessary laboratory facilities for analysis. Not forgetting my course mates for their patient and guidance to help me in completed the research.

My acknowledgements would not be completed without mentioning my family for their positive encouragement and continuous support, without whom I would barely be who I am.

Last but no least, financial support from Unimas seed grant under Grant No. 1/42/322/2002 (59) is gratefully acknowledged.

TABLE OF CONTENTS

DECLARATION	ii
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	iv
LISTS OF FIGURES	vi
LISTS OF TABLES	vii
ABSTRACT	viii
ABSTRAK	ix
CHAPTER ONE INTRODUCTION	
1.1 Gallium	1
1.2 Chalcone	3
1.3 Schiff base	5
1.4 Objectives	8
CHAPTER TWO MATERIALS AND METHODS	
2.1 Experimental	9
2.2 Synthesis of chalcone	9
2.2.1.a 1-phenyl-3(2-hydroxy-phenyl)-propenone (L1)	9
2.2.1.b Purification of L1	10
2.2.2 Synthesis and Purification of L2	10
2.3 Synthesis of gallium complexes by gallium(III) bromide with chalcone	
2.3.1 Synthesis of GaBr ₃ .L1	10
2.3.2 Synthesis of GaBr ₃ .L2	10

2.4 Synthesis of Schiff base	11
2.4.1.a Synthesis of 4-[(4-Chloro-phenylimino)-methyl]-phenol,L3	11
2.4.1.b Purification of L3	11
2.4.2 Synthesis and Purification of L4	11
2.4.3 Synthesis and Purification of L5	11
2.5 Synthesis of gallium(III) complexes by gallium(III) bromide with Schiff base	12
2.5.1 Synthesis of GaBr ₃ .L3	12
2.5.2 Synthesis of GaBr ₃ .L4 GaBr ₃ .L5	12
2.6 Characterization	12
CHAPTER THREE RESULTS	
3.1 Physical & Analytical data	13
3.2 & 3.3 FT-IR of ligand and complexes	14
3.4 & 3.5 ¹ H NMR data of ligand and complexes	14
CHAPTER FOUR DISCUSSION	
4.1 Complexation study of GaBr ₃ with L1 (GaBr ₃ .L1)	15
4.2 Complexation study of GaBr ₃ with L2 (GaBr ₃ .L2)	16
4.3 Complexation study of GaBr ₃ with L3 (GaBr ₃ .L3)	18
4.4 Complexation study of GaBr ₃ with L4 (GaBr ₃ .L4)	21
4.5 Complexation study of GaBr ₃ with L5 (GaBr ₃ .L5)	23
CHAPTER FIVE CONCLUSION	26
RECOMMENDATION	
REFERENCES	
APPENDICES	

LIST OF FIGURES

Figure 1.2.1: Claisen-Smith Reaction	3
Figure 1.2.2: Tautomerization of chalcone	4
Figure 1.2.3: Postulated structure of InBr_3 with 2-hydroxychalcone	4
Figure 1.3.1: Postulated complex structure of InBr_3 with 3-chlorosalicylideneaniline	5
Figure 1.3.2: Postulated complex structure of Bu_3SnCl with 3-chlorosalicylideneaniline	6
Figure 1.3.3: Complex of SnCl_4 and salicylideneaniline	6
Figure 1.3.4: Complex of SnCl_2 with salicylideneaniline	7
Figure 1.4.1: Chalcone (L1-L2) and Schiff base (L3-L5)	8
Figure 4.1.1: Tautomerization reaction of L1 in solvent system of ethanol	15
Figure 4.1.2: Postulated complex structure of $\text{GaBr}_3\cdot\text{L1}$	16
Figure 4.2.1: Tautomerization reaction of L2 in solvent system of ethanol	17
Figure 4.2.2: Postulated complex structure of $\text{GaBr}_3\cdot\text{L2}$	18
Figure 4.3.1: Formation of intermolecular hydrogen bond resulting by dimerization of L3	19
Figure 4.3.2: Postulated complex structure of $\text{GaBr}_3\cdot\text{L3}$	20
Figure 4.4.1: Formation of intramolecular hydrogen bond during complexation with GaBr_3	22
Figure 4.4.2: Postulated complex structure of $\text{GaBr}_3\cdot\text{L4}$	23
Figure 4.5.1: Formation of intramolecular hydrogen bond during complexation with GaBr_3	24
Figure 4.5.2: Postulated complex structure of $\text{GaBr}_3\cdot\text{L5}$	25

LIST OF TABLES

Table 3.1: Physical and Analytical data	13
Table 3.2: Main IR data of ligand L1 and L2 and their complexes (cm ⁻¹) ^a	14
Table 3.3: Main IR data of ligand L3-L5 and its complexes (cm ⁻¹) ^a	14
Table 3.4: ¹ H NMR data of the ligand L1-L2 and their complexes (δ, ppm) ^b	14
Table 3.5: ¹ H NMR data of the ligand L3-L5 and their complexes (δ, ppm) ^b	14

ABSTRACT

Synthesis and spectroscopic characterization of gallium(III) complexes with chalcone and Schiff base are reported in this thesis. Tautomerization was happening in chalcone before coordinated with gallium(III) bromide. For Schiff base compounds, which OH group located in *ortho*- or *para*- substitution, a intramolecular hydrogen bond present between hydrogen atom from phenolic group with nitrogen atom from C=N group. Reactions of chalcone as well as Schiff base with gallium(III) bromide gave a new respective coordination mode of Ga-O bonds. The ligands appear to act as monodentate species in Ga(III) complexes, making gallium atom four-coordinated in tetrahedron structure. The ratio between Ga : ligand is 1:1 for all the Ga(III) complexes in this research.

Key words: Chalcone, Schiff base, tautomerization, gallium(III) complex, Ga-O

ABSTRAK

Sintesis dan pencirian spektroskopi bagi kompleks gallium(III) dengan dua siri ligan iaitu kalkon dan bes Schiff telah dilaporkan dalam tesis ini. Pentautomeran berlaku di dalam kalkon sebelum berkoordinat dengan gallium(III) bromida. Bagi sebatian bes Schiff, di mana kumpulan OH terletak pada penukargantian orto atau para, ikatan hidrogen intramolekul hadir antara atom hidrogen dari kumpulan fenolik dengan atom nitrogen dari kumpulan C=N. Tindak balas kalkon dan bes Schiff dengan gallium(III) bromida masing-masing menghasilkan mod koordinatan yang baru iaitu ikatan Ga-O. Ligan wujud sebagai spesies monodentat dalam kompleks gallium(III). Dengan itu, atom gallium membentuk nombor koordinatan 4 dalam struktur tetrahedron. Nisbah antara Ga : ligan ialah 1:1 bagi semua kompleks gallium(III) dalam kajian ini.

Kata kunci: Kalkon, bes Schiff, pentautomeran, kompleks gallium(III), Ga-O

CHAPTER ONE: INTRODUCTION

1.1 Gallium

Gallium is an element of Group IIIA in periodic table. Its atomic number is 31 with a atomic weight of 69.72. The electron configuration of Ga is $[\text{Ar}]3d^{10}4s^24p^1$ and is classified among rare and trace elements (Sheka, 1966).

In its chemical properties, gallium is superficially oxidized in air and oxygen, and loses its luster becoming coated with a thin film of a grayish-blue oxide. (Sheka, 1966). The stable charge state of gallium is +3, but it is also found in the unipositive +1 and bipoisitive +2 states such as gallium monobromide (GaBr), gallium dibromide (GaBr_2) and gallium tribromide (GaBr_3) (Elschenbroich, 1992). Compounds of Ga^+ and Ga^{2+} are less stable than those of Ga^{3+} , and their salt have reducing properties (Sheka, 1966).

Klemm and Tilk have synthesized gallium(III) bromide by passing nitrogen or carbon dioxide saturated with bromine over gallium. Gallium(III) bromide is colourless, hygroscopic and crystalline with melting point given is 122.5°C and the boiling point is 279°C (Sheka, 1966).

Gallium achieves an oxidation state of 3 by forming covalent compounds via $ns \rightarrow np$ promotion (Massey, 2000). Gallium has coordination numbers of 4, 5 or 6 depending on the number of added ligands [dioxane, pyridine, triethylphosphine or halide] which can be represented by GaX_3L , GaX_3L_2 and GaX_3L_3 [L = ligands and X = halides groups] (Massey, 2000). With the exception of iodine, the halogens react with gallium readily, even in the cold condition to form GaX_n [X = fluorine, chloride, bromine; $n = 1, 2$ and 3] (Dohmeier, 1996).

A wide variation in stereochemistry and ligand type have been found among the many complexes of gallium. Octahedral cations ML_6^{3+} are formed by the gallium when L is a monodentate ligand such as water, dimethylsulfoxide or dimethylformamide. However,

complexes of the halides are by far the most numerous and almost invariably have tetrahedral, trigonal bipyramidal or octahedral coordination (Messey, 2000). Gallium complex with coordination number of 5 represented by GaX_3L_2 has trigonal bipyramidal structure. It is experimental confirmation by Veitis and Palenik (1969) through X-ray crystallography (Yee and Jones, 1969). Another structure of Gallium complex with coordination number of 5 is tetragonal pyramidal.

In the last few years, vigorous development in the semi-conductor electronic and other new technical fields has resulted in a broad expansion of research in the chemistry and technology of gallium and its compounds. Gallium is undoubtedly find extensive application as a material for the preparation of rectifiers, crystal amplifiers and spacistors in electrical engineering and semiconductor device manufacturing (Krik-Othener, 1995). According to Steven (2002), gallium arsenide (GaAs) has better electrical characteristics than silicon in electrical engineering and semiconductor device manufacturing. Gallium, with a boiling point of about 2030°C, has the longest liquid range of all the elements and has been used in high-temperature thermometers (Massey, 2000). The alloys Ga-Zn, Ga-Cd or Ga-Al are employed instead of mercury; the light is richer in blue and red rays. Radiation from such lamps has a desirable therapeutic effect.

1.2 Chalcone

Benzylideneacetophenone or its common name chalcone, is one of the familiar natural pigment introduced by Kostanecki in 1899. Chalcones are important key precursors in the synthesis of various flavonoids as they can be transform easily in flavanones by cyclization in acidic medium, in flavones or aurones by oxidative cyclization in presence of hydrogen peroxide in basic medium or other oxidants (Bose, 2001).

There are several methodologies for the synthesis of chalcone. However, chalcone is usually synthesized through Claisen-Schmidt reaction in basic condition (Eddarir, 2003). These method involves condensation reaction of acetophenone and benzaldehyde under basic medium to form α,β -unsaturated ketones which has shown in Figure 1.2.1 (Furniss et al., 1989).

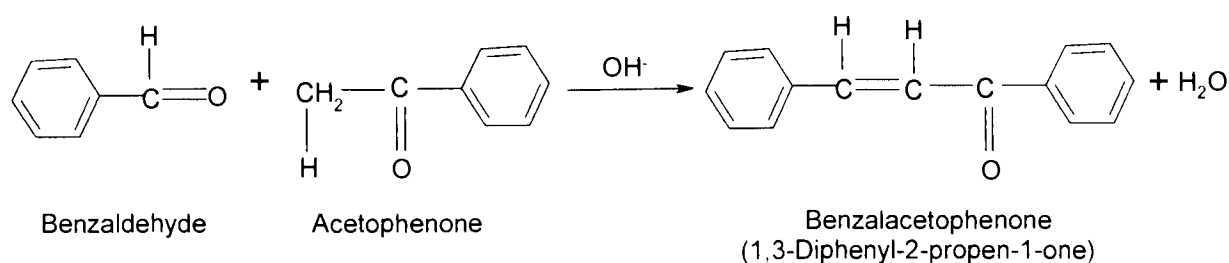
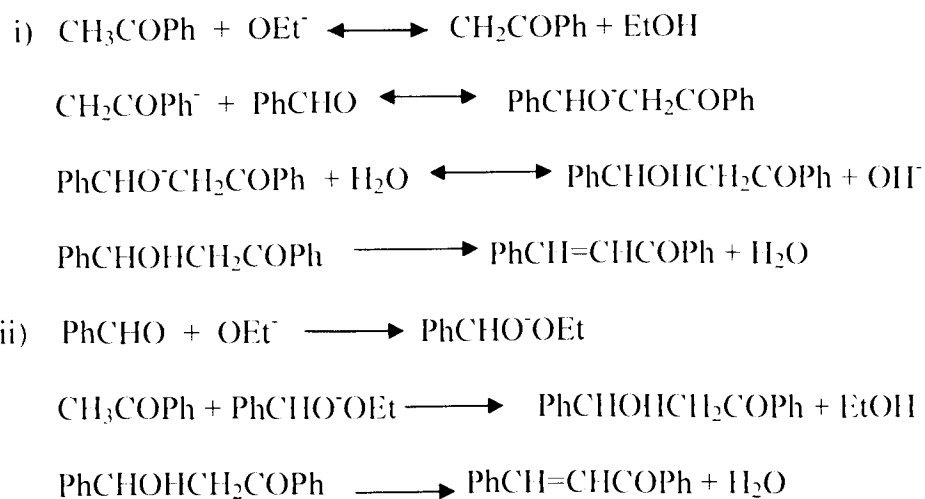


Figure 1.2.1: Claisen-Schmidt Reaction

The general accepted mechanisms involve the following steps: (Nayak & Rout, 1975)



Tay (1999) reported that indium(III) bromide reacted with 2-hydroxychalcone can form In-O bond in tetrahedron geometry. It was interesting to note that tautomerization was happened in chalcone before coordinated with InBr_3 and the reaction is shown in Figure 1.2.2.

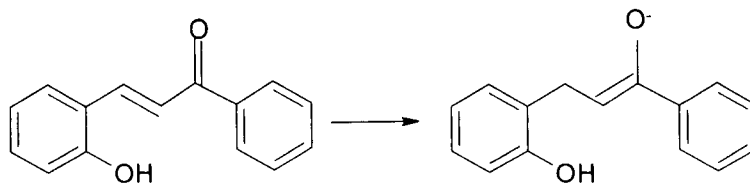


Figure 1.2.2: Tautomerization of chalcone

The postulated structure of InBr_3 with 2-hydroxychalcone is shown in Figure 1.2.3.

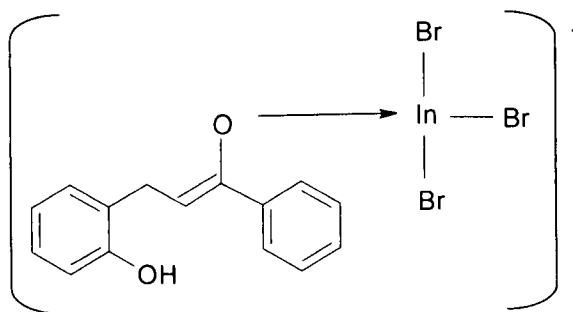


Figure 1.2.3: Postulated structure of InBr_3 with 2-hydroxychalcone

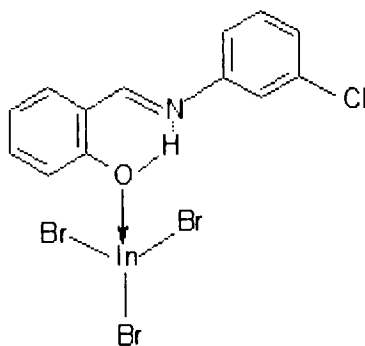
Chalcones bearing non natural substituents have been synthesized during the recent years in order to develop drugs active against cancer, malaria, leishmaniase, tuberculosis and cardiovascular diseases (Eddarir et al., 2003). Chalcones and its derivatives also play an important role in photochemistry. They are applied in photo-alignment layer of liquid crystal display since they possess high photo-reactivity can combine with polyimide to facilitate the photoreaction and generate stable alignment layers (Song et al., 2002).

1.3 Schiff Base

The presence of C=N double bonds in a molecule is classified as Schiff base. Schiff base is synthesized by the reaction between primary amine with carbonyl group of aldehyde or

ketone which has empirical formula $\begin{matrix} R \\ \diagdown \\ C = N - R'' \\ \diagup \\ R' \end{matrix}$ where R, R' and R'' represented alkyl,

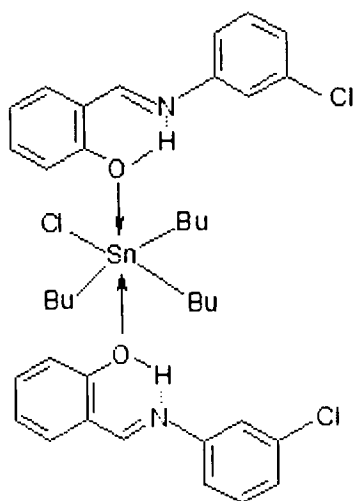
allyl and aryl (Tay, 1999). Indium(III) bromide reacted with 3-chlorosalicylideneaniline can form In-O bond in tetrahedron geometry structure and it behaves as a monodentate ligand to the complex (Tay, 1999). The postulated structure of InBr₃ with 3-chlorosalicylideneaniline is shown in Figure 1.3.1.



----- Intramolecular hydrogen bond

Figure 1.3.1: Postulated complex structure of InBr₃ with 3-chlorosalicylideneaniline

By using the same Schiff base ligand, another experiment investigated by Tay proposed the reaction of tributyltin(IV) chloride with 3-chlorosalicylideneaniline, which afforded the six-coordinate complex with octahedral structure, which has shown in Figure 1.3.2 (Tay, 1999).



----- Intramolecular hydrogen bond

Figure 1.3.2: Postulated complex structure of Bu_3SnCl with 3-chlorosalicylideneaniline

Schiff base has a special characteristic since it can behave as monodentate, bidentate, tridentate and tetradentate. Kogan and his co-workers have studied the reactivity of stanum(IV) chloride with salicylideneaniline to give Sn-N bond. Salicylideneaniline behaved as a monodentate ligand when coordinated with Sn and formed a six coordination Sn complex, which as represented in Figure 1.3.3 (Kogan et al., 1965).

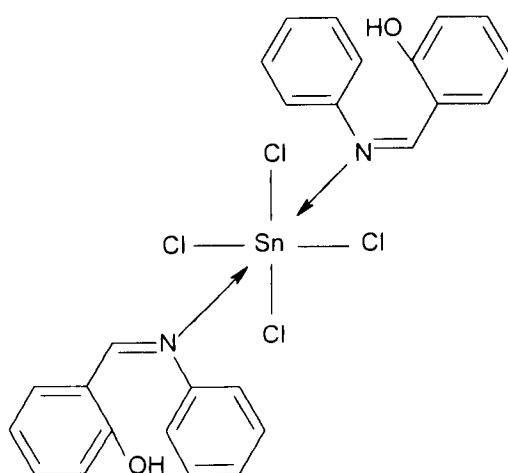


Figure 1.3.3: Complex of $SnCl_4$ and salicylideneaniline

Biradar and his co-workers had successfully investigated complex of SnCl_2 with salicylideneaniline through UV, infrared and NMR analyses methods. This schiff base behaves as a bidentate ligand, which has shown in Figure 1.3.4.

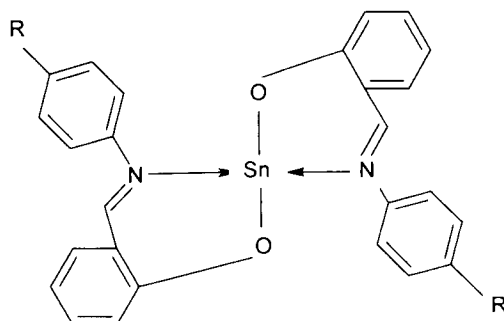


Figure 1.3.4: Complex of SnCl_2 with salicylideneaniline

Tridentate ligand can be prepared by the condensation reaction of 2-hydroxybenzaldehyde with ethylenediamine. This kind of ligand favorably coordinated with chromium, cobalt and iron (Benson, 1977). Tridentate ligand can behave by asymmetry Schiff base, for example, salicylaldehydacetonylenediamine, where tridentate ligand form complexes with nickel(II) and palladium(II) (Kwiatkowski, 1980).

Aromatic Schiff base compounds of the salicylidene-aminophenol type had been studied as useful fluorimetric reagents for aluminium, gallium, indium, scandium and beryllium (Morisigie, 1974). For example, *o,o'*-dihydroxy Schiff base compounds in analogy with *o,o'*-dihydroxyazo compounds form fluorescent gallium complexes (Hiraki, 1972).

1.4 Objectives

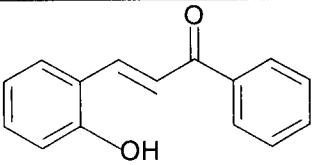
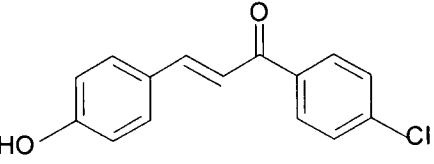
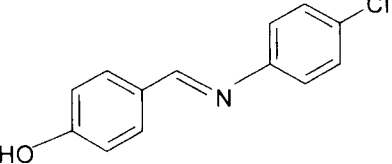
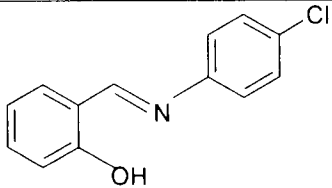
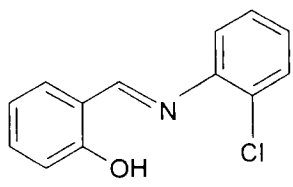
	1-phenyl-3(2-hydroxy-phenyl)-propenone (L1)
	1-(4'-chloro-phenyl)-3(4-hydroxy-phenyl)-propenone (L2)
	4-[(4-Chloro-phenylimino)-methyl]-phenol (L3)
	2-[(4-Chloro-phenylimino)-methyl]-phenol (L4)
	2-[(2-Chloro-phenylimino)-methyl]-phenol (L5)

Figure 1.4.1: Chalcone (L1-L2) and Schiff base (L3-L5)

This study serves to two purposes. First, to synthesis the gallium (III) complexes by reacting with the two series ligands, respectively. Second, to characterize the complexes using FTIR, $^1\text{H-NMR}$, CHN and UV-spectroscopy. Mode coordination and complexes structures are determined from the analysis data.

CHAPTER TWO: MATERIALS AND METHODS

2.1 Experimental

Ethanol 99.8% (gred A.R) and acetone (gred A.R) were obtained from R & M Chemicals.

Others chemicals are:-

- a. 4'-chloroacetophenone 97%
- b. 4-chloroaniline 99%
- c. 2-chloroaniline 98%
- d. Benzaldehyde
- e. 2-hydroxybenzaldehyde 99%
- f. 4-hydroxybenzaldehyde 99%
- g. Gallium (III) bromide 99.999%

All chemical were obtained from Acros, Aldrich Chemicals and BDH chemicals Limited.

2.2 *Synthesis of chalcone*

2.2.1.a *1-phenyl-3(2-hydroxy-phenyl)-propenone (L1)*

Potassium hydroxide, KOH, (1.00 g, 0.018 moles) was dissolved into 10 mL ethanol 95 % in a 250 mL conical flask. Put the solution at room temperature. Added acetophenone (0.48 g, 0.004 moles) into the solution followed by 2-hydroxybenzaldehyde (0.50 g, 0.004 moles). The solution was stirred for 3 hr before cold it in the ice bath. At the end of the reaction, 8 M of HCl was added in drop by drop until it formed acidic condition. Light yellow solid precipitates were obtained. Filtered the precipitates with Funnel filter and dried in desiccator. Yield, 0.84 g, 75 %.

2.2.1.b Purification of L1

L1 was purified by crystallization from 50 mL 95% hot ethanol (60 - 70 °C). The beaker was closed with aluminum foil paper. After 1 week, crystal was formed. Collected it and dried in desiccator.

2.2.2 Synthesis and Purification of L2

The procedure of synthesis and purification of L2 is similar to the procedure of synthesis L1 as described in Section 2.2.1.a and 2.2.1.b but 2-hydroxybenzaldehyde was replaced by 4-hydroxybenzaldehyde (0.50 g, 0.004 moles) and acetophenone was replaced by 4'-chloroacetophenone (0.62 g, 0.004 moles). Yield, 0.51 g, 63 %.

2.3 Synthesis of gallium complexes by gallium(III) bromide with chalcone

2.3.1 Synthesis of GaBr₃.L1

L1 (0.836 g, 0.003 moles), triethylamine (0.327 g, 0.003 moles), 16 mL of ethanol 99.8 % and gallium(III) bromide (1.00 g, 0.003 moles) were added into a 100 mL three neck round bottom flask and stirred the mixture until a homogeneous aqueous phase formed. The solution was refluxed for four hr under nitrogen condition at a temperature of 94 °C. Upon cooling process, the extra solvent was evaporated through a rotor vapor and brown-colour solid was formed. This solid was separated out, through filtration and dried in a desiccator. Yield, 0.94 g, 52 %.

2.3.2 Synthesis of GaBr₃.L2

The procedure of synthesis GaBr₃ with L2 is similar to the procedure as described in Section 2.3.1 but L1 was replaced by L2 (0.776 g, 0.003 moles). Yield, 0.85 g, 48 %.

2.4 *Synthesis of Schiff base*

2.4.1.a *Synthesis of 4-[(4-Chloro-phenylimino)-methyl]-phenol, L3*

4-chloroaniline (1.3 g, 0.01 moles) was measured and dissolved into 10 mL ethanol 95 %. 4-hydroxybenzaldehyde (1.2 g, 0.01 moles) was added into the solution and stirred for one hr. The gray precipitate obtained was filtered by Funnel filter and dried in dessicator. Yield, 2.05g, 82 %.

2.4.1.b *Purification of L3*

L3 was purified by crystallization from 50 mL 95 % hot ethanol (60 – 70 °C). The beaker was closed with aluminium foil paper. After 1 week, gray-colour crystal was formed. Collected it and dried in desiccator.

2.4.2 *Synthesis and purification of L4*

The procedure of synthesis and purification of L4 is similar to the procedure of synthesis L3 as described in Section 2.4.1.a and 2.4.1.b but 4-hydroxybenzaldehyde was replaced by 2-hydroxybenzaldehyde (1.2 g, 0.01 moles) . Yield, 1.25 g, 63 %.

2.4.3 *Synthesis and purification of L5*

The procedure of synthesis and purification of L5 is similar to the procedure of synthesis L4 but 4-chloroaniline was replaced by 2-chloroaniline (1.3 g, 0.01 moles). Yield, 1.70 g, 79 %.

2.5 Synthesis of gallium(III) complexes by gallium(III) bromide with Schiff base

2.5.1 Synthesis of GaBr₃.L3

L3 (0.743 g, 0.003 moles), 16 mL of 99.8 % ethanol and gallium(III) bromide (1.00 g, 0.003 moles) were added into a 100 mL round bottom flask. The mixture solution was stirred until it formed a homogeneous phase and refluxed for four hr under nitrogen atmosphere at a temperature of 94 °C. Dark brown solid particles were formed during the cooling process. Filtered out the solid particles and dried in the desiccator. Yield, 0.78 g, 45 %.

2.5.2 Synthesis of GaBr₃.L4 and GaBr₃.L5

The procedure of synthesized GaBr₃.L4 and GaBr₃.L5 was similar to the procedure as described in section 2.5.1 but L3 was replaced by L4 (0.743 g, 0.003 moles) and L5 (0.743 g, 0.003 moles), respectively. Yield, 0.89 g, 51 %. Yield, 0.80 g, 46 %.

2.6 Characterization

Infrared spectra were recorded on Shimadzu 8001PC Fourier-Transform Infrared Spectrometer with wavelength range between 4000 and 400 cm⁻¹. Samples in powder form were pressed into disks using spectroscopically pure KBr. ¹H NMR spectra were recorded in acetone-d and CDCl₃ solution on a Advance 300 MHz Bruker FT-NMR Spectrometer. Percentages of C, H & N were recorded using Perkin Elmer CHN Series II 2400.

CHAPTER THREE: RESULTS

The appearance and elemental analytical data of L1 – L5 and their complexes are presented in

Table 3.1 whereas IR data are recorded in Table 3.2 and Table 3.3.

Table 3.1: Physical and Analytical data

Compound	Formula	Color	M.P. (°C)	Found (Calcd.) %		
				C	H	N
L1	C ₁₅ H ₁₂ O ₂	Light yellow	194.5 – 195.5	67.74 (80.36)	4.32 (5.36)	–
GaBr ₃ .L1	C ₁₅ H ₁₃ O ₂ GaBr ₃	Brown	167.6 – 169.7	38.46 (33.74)	3.34 (2.44)	0.97 –
L2	C ₁₅ H ₁₁ O ₂ Cl	Light brown	163.0 – 164.8	65.28 (69.63)	4.22 (4.26)	–
GaBr ₃ .L2	C ₁₅ H ₁₂ O ₂ ClGaBr ₃	Red brown	109.5 – 120.0	26.70 (31.64)	2.91 (2.11)	1.39 –
L3	C ₁₃ H ₁₀ NOCl	Gray	189.5 – 189.6	67.01 (67.39)	3.96 (4.32)	6.20 (6.05)
GaBr ₃ .L3	C ₁₃ H ₁₀ NOClGaBr ₃	Dark brown	119.5 – 120.5	24.94 (28.84)	2.09 (1.85)	2.10 (2.59)
L4	C ₁₃ H ₁₀ NOCl	Light golden	103.5 – 103.7	66.97 (67.39)	3.89 (4.32)	6.20 (6.05)
GaBr ₃ .L4	C ₁₃ H ₁₀ NOClGaBr ₃	Yellow	261.0 – 263.0	30.60 (28.84)	1.88 (1.85)	2.62 (2.59)
L5	C ₁₃ H ₁₀ NOCl	Light yellow	78.7 – 78.9	67.30 (67.39)	3.97 (4.32)	6.44 (6.05)
GaBr ₃ .L5	C ₁₃ H ₁₀ NOClGaBr ₃	Red brown	85.6 – 86.0	26.61 (28.84)	2.00 (1.85)	2.21 (2.59)

Table 3.2: Main IR data of ligand L1 and L2 and their complexes (cm^{-1})^a.

Compound	ν_{OH}	$\nu_{\text{C-H}}$	$\nu_{\text{C}=\text{C}}$	$\nu_{\text{C}=\text{O}}$	$\nu_{\text{Ga-O}}$
L1	3250br	-	1645m	1645m	-
GaBr ₃ .L1	3356br	2980s	1647m	1647m	628m
L2	3240s	-	1647m	1690m	-
GaBr ₃ .L2	3358br	2987w	1650m	1660m	628m

Table 3.3-Main IR data of ligand L3-L5 and its complexes (cm^{-1})^a.

Compound	ν_{OH}	$\nu_{\text{C}=\text{N}}$	$\nu_{\text{N-H}}$	$\nu_{\text{Ga-O}}$
L3	3200-3400w	1600s	3100w	-
GaBr ₃ .L3	3200w	1651s	3100w	777m
L4	3200-3400br	1640w	3100w	-
GaBr ₃ .L4	3100-3400w	1645m	3150w	630m
L5	3200-3400br	1639w	3100w	-
GaBr ₃ .L5	3300br	1639m	3100w	580m

^a As compressed KBr disc

* Not observed

w = weak, m = medium, s = strong, mw = medium weak, br = broad

Table 3.4-¹H NMR data of the ligand L1-L2 and their complexes (δ , ppm)^b

Compound	δ_{CHarom}	$\delta_{\text{HC}=\text{C}}$	$\delta_{\text{HC}=\text{C}-\text{C}}$	δ_{OH}
L1	7.60-7.80m	8.15d	-	*
GaBr ₃ .L1	7.60-7.76m	6.86d	3.10s	10.14s
L2	7.50-7.90m	8.16d	-	10.13s
GaBr ₃ .L2	7.51-7.94m	6.60t	3.10s	10.14s

Table 3.5-¹H NMR data of the ligand L3-L5 and their complexes (δ , ppm)^b

Compound	$\delta_{\text{OH-N}}$	$\delta_{\text{CH}=\text{N}}$	δ_{CHarom}
L3	10.61s	8.47d	7.11-7.86m
GaBr ₃ .L3	*	8.51s	6.74-7.82m
L4	13.04s	8.61s	6.94-7.44m
GaBr ₃ .L4	12.85s	8.96s	6.96-7.67m
L5	13.23s	8.64s	6.94-7.52m
GaBr ₃ .L5	10.26s	9.03s	6.98-7.60m

* Not observed

s = singlet, d = doublet, t = triplet, m = multiplet δ values to high frequency to TMS

^b Measured at 400 MHz in acetone-d and CDCl₃ solution

CHAPTER FIVE: DISCUSSION

4.1 Complexation study of GaBr₃ with L1 (GaBr₃.L1)

The IR data of GaBr₃.L1 in Table 3.2 showed a new strong absorption band at 2980 cm⁻¹ is due to the C-H stretching frequency (Pavia et al., 2001). This band is clearly absent in the IR spectrum of L1. This absorption band showed that tautomerization was happened in L1 before coordinated with GaBr₃ (Dhar, 1981). During tautomerization, the double bond arrangement was transferred from C₇ and C₈ to C₈ and C₉. Tautomerization reaction of L1 is shown in Figure 4.1.1.

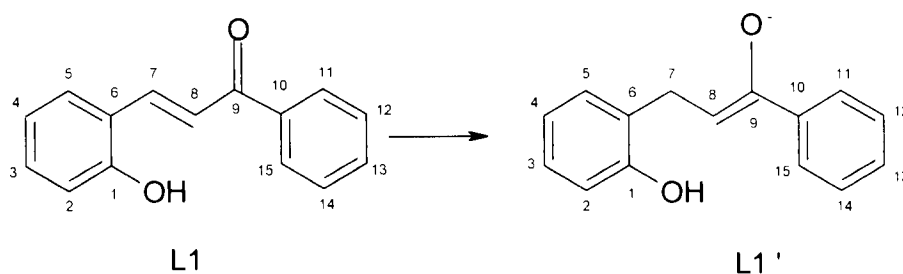


Figure 4.1.1: Tautomerization reaction of L1 in solvent system of ethanol

Comparison of the ¹H NMR spectra for complex and L1 offers further evidence, a singlet of HC-C₇=C₈ appeared obviously at δ 3.37 (2H) in complex spectra. This indicated that C₇ with sp³ hybridized in GaBr₃.L1 complex. Additionally, the ¹H NMR spectra of L1 showed a duplet at δ 7.65 which assigned to HC-C=O (Silva et al., 1999 and Nanette et al., 1999). For ¹H NMR spectra of GaBr₃.L1, this doublet was changed to triplet which indicated that two neighboring protons presented L1 become L1' through tautomerization. This reaction suggested that oxygen atom at C₉ with one negative charge was formed. This electron-rich oxygen has high tendency to coordinate with the gallium atom, which is electropositive and expected the formation of Ga-O bond (Shuki et al., 1992). The IR spectra showed a medium absorption band due to Ga-O at 628 cm⁻¹ which cannot be found in the IR spectra of L1 (Ilieva et al., 2001). This absorption band represented a new coordination mode of Ga-O during the complexation of GaBr₃.L1.