# PREPARATION AND CHARACTERIZATION OF SOME POLYDENTATE ORGANIC LIGANDS AND THEIR CHELATES WITH SOME TRANSITION METALS

**Thesis Submitted By**

**Ahmed Badr Kamel Mohamed Gad**

**(B.Sc.; Chem.-Geo., Cairo University; 2006)**

**A Thesis Submitted For the Partial Fulfillment of**
**The M.Sc. Degree**
**In**
**Inorganic Chemistry**

**To**
**Chemistry Department**
**Faculty of Science - Cairo University**

**(2009)**

# تحضير و توصيف بعض المركبات العضوية عديدة العطاء و متراكباتها مع بعض العناصر الانتقالية

رسالة مقدمة
إلى
كلية العلوم
جامعة القاهرة

من الطالب
أحمد بدر كامل محمد جاد
بكالوريوس العلوم (كيمياء- جيولوجيا)
(٢٠٠٦)
جامعة القاهرة

للحصول على درجة الماجستير
في
الكيمياء غير العضوية
(٢٠٠٩)

# ACKNOWLEDGMENT

**All gratitude is due to ALLAH for guiding and aiding me to bring forth to light this thesis.**

**I would like to express my deep thanks and full gratitude to Prof. Dr. Mohamed A. Badawy, Prof. of Organic Chemistry, Prof. Dr. Gehad G. Mohamed, Prof. of Inorganic Chemistry and to Prof. Dr. Mohamed M. Omar, Prof. of Inorganic Chemistry, Chemistry Department, Faculty of Science, Cairo University for suggesting this research project, supervision, perfect guidance, continuous support and helpful comments which were indispensable to the completion of the present work.**

**Finally, I would like to thank all my colleague in the department of chemistry, who helped me in the preparation and completion of this work.**

***Ahmed Badr***

## ABSTRACT

**Name:** Ahmed Badr Kamel Mohamed Gad.
**Title of Thesis:** Preparation and characterization of some polydentate organic ligands and their chelates with some transition metals.
**Degree: (M.Sc):** Master of Science in Inorganic Chemistry, Faculty of Science, Cairo University, 2009.

This work had been carried out to investigate the coordination behaviour of three organic ligands with different coordination sites, towards some bi- and trivalent metal ions like Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Fe(III) The solid chelates of ($HL^1$), ($H_2L^2$) and ($HL^3$) were prepared and subjected to many analytical techniques such as elemental analyses, IR, $^1H$ NMR and solid reflectance spectra, magnetic moment, molar conductance, and thermal analyses techniques. The chelates were found to have octahedral geometry. The ligands ($HL^1$, $H_2L^2$ and $HL^3$) and their binary chelates were subjected to thermal analyses (DTA, DTG and TG) and the different activation thermodynamic parameters, namely $E^*$, $\Delta H^*$, $\Delta S^*$ and $\Delta G^*$ were calculated from their corresponding DTG curves to throw more light on the nature of changes accompanying the thermal decomposition process of these complexes. The biological activity of the organic ligands and their complexes were also screened.



**Key Words:** Organic ligands complexes, Elemental analyses, Spectroscopy, Thermal analyses, Biological activity.


Supervisors: Prof. Dr. Mohamed. A. Badawy, Signatures:
Prof. Dr. Gehad G. Mohamed,
Prof. Dr. Mohamed M. Omar.

**Prof. Dr. Mohamed M. shoukry**

Chairman of Chemistry Department
Faculty of Science, Cairo University

# AIM OF THE PRESENT WORK

The importance of chelation behaviour of organic ligands with the biologically essential metal ions has been emphasized in this thesis. The various researches appearing in the literature on chelation tendency of organic ligands and also the study of the complexation equilibria of binary and ternary systems, involving metal ions and organic ligands in the presence of different secondary ligands has given useful information for elucidation of the biological activity of these organic ligands. Thus combination of recent experimental and theoretical developments can help chemists to develop innovative strategies for preparing improved and better biologically active organic ligands in the light of the chelate hypothesis**.**

The present investigation aims chiefly to study the nature of the chelates formed as the result of the interaction between some new organic ligands of different donor sites like bipositive and tripositive metal ions. The solid chelates of ($HL^1$), ($H_2L^2$) and ($HL^3$) ligands with Fe(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions are prepared and subjected to many analytical techniques such as IR, $^1$H NMR and solid reflectance spectra, magnetic moment, molar conductance, and thermal analyses techniques.

The involvement of the different coordination sites of the ligands under study in binding to the metal ions is elucidated by comparing the IR spectra of the free ligands with those of their metal chelates. The solid reflectance spectra and magnetic moment measurements of the chelates are studied to throw more light on their geometrical structures and nature of bonding between the ligands and metal ions. The molar conductance technique is utilized to show the electrolytic nature of the chelates.

The ligands ($HL^1$, $H_2L^2$, and $HL^3$) and their binary chelates are subjected to thermal analyses (TG, DTG and DTA) in order to confirm the proposed molecular formulae of the chelates and show the mechanism of thermal decomposition of the ligands under study. The different activation

thermodynamic parameters, namely: $E^*$, $\Delta H^*$, $\Delta S^*$ and $\Delta G^*$ are calculated from their corresponding DrTGA curves to throw more light on the nature of changes accompanying the thermal decomposition process of these complexes. The ligands under investigation together with their metal chelates are screened for their biological activity against insecticides.

# INTRODUCTION

It is very clear that, by selecting suitable metal ions and ligands and carrying out reactions in suitable single or mixed solvent medium under proper selected conditions, one can dictate the formation of a desired chelate compound. When once the complex is isolated under proper conditions, its complete characterization offers great efforts. One should be able to obtain convincing information regarding (i) oxidation number of the metal ion, (ii) its coordination number and (iii) stereochemistry of the complex. A large number of physicochemical measurements including IR, magnetic susceptibility, electronic and mass spectra, $^{1}$HNMR, molar conductance and thermal analyses (TGA, DTA) measurements,… etc are required to get fairly safe conclusions. Once a complex is characterized, it becomes a material for a host of investigations.

Organic ligands and their metal complexes are a widely studied subject because of their industrial and biological applications. Therefore, the main objective of this thesis is the isolation and characterization of the metal complexes of the organic ligands under study. Different physico-chemical, spectroscopic and thermal methods of analyses are utilized to characterized the ligands under investigation and their chelates in addition to studying their biological activity.

# Literature Survey

# Results and Discussion

# Experimental

# Arabic summary

# الملخص العربي

"وَعَلَّمَكَ مَا لَمْ تَكُنْ تَعْلَمُ وَكَانَ فَضْلُ اللّهِ عَلَيْكَ عَظِيماً"

**صدق الله العظيم**

**النساء ١١٣**

# English Summary

# المستخلص


الاسم : أحمد بدر كامل محمد جاد

عنوان الرسالة : "تحضير وتوصيف بعض المركبات العضوية عديدة العطاء ومتراكباتها مع بعض العناصر الانتقالية "

الدرجة : ماجستير(الكيمياء غير العضوية)

تهدف هذه الدراسة إلى معرفة طريقة الارتباط التساهمى بين بعض المركبات العضوية: ٣-(٢-إكزو-٢-بارا-توليليثيل) كينواكزالين-٢(١H)-ون ($HL^1$)، ٣-(٢-(٢-داى كلوروبينزليدين)هيدرازينيل)-٤-إكزو-٤,٥-داي هيدرو ثيازول-٥-ويل) اسيتيك اسيد($H_2L^2$),٣-بينزيل-(H٤)-(١,٣,٤) ثيادايازولو [C-٢,٣] [١,٢,٤] ترايازين-٤-ون($HL^3$)وبعض أيونات العناصر الانتقالية: الكوبلت والنيكل والنحاس والخارصين والمنجنيز ثنائية التكافؤ وأيون الحديد ثلاثي التكافؤ. تم حساب ثوابت التأين بالطرق الطيفية للمركبات العضوية قيد الدراسة عند درجه حرارة ٢٥ درجة مئوية في خليط من الكحول الإيثيلى بنسبة حجمية ٥٠ % كذلك تم حساب ثوابت استقرار متراكبات المركبات العضوية مع العناصر المذكورة آنفا. تم فصل متراكبات المركبات العضوية مع العناصر المذكورة فى الصورة الصلبة وأجرى تحليل كيميائي دقيق لهذه المتراكبات بالإضافة إلى أطياف الإمتصاص التذبذى فى مدى الآشعه الحمراء والرنين النووى المغناطيسى والطيف الكتلي والتحليل الحراري وقد أمكن اقتراح التركيب التناسقى لهذه المتراكبات بناءً على القياسات المذكورة. كما تم حساب رتب ميكانيكية التفكك الحراري وحساب الثوابت الديناميكية الحرارية. تم أيضا دراسة النشاط البيولوجي للمركبات العضوية ومتراكباتها.



الكلمات الدالة: متراكبات المركبات العضوية، قياس الأس الهيدروجيني، التحليل العنصري، التحليل الطيفي، التحليل الحراري، العناصر الانتقالية، النشاط البيولوجي.


المشرفون :

١. أ.د/ محمد أحمد بدوى — التوقيع

٢. أ.د/ جهاد جنيدى محمد

٣. أ.د/ محمد محمد عمر

ا.د/ محمد محمد شكرى

رئيس مجلس قسم الكيمياء
كلية العلوم – جامعة القاهرة