Mona maghraby

بسم اللّه الرحمن الرحيم

مركز الشبكات وتكنولوجيا المعلومات

قسم التوثيق الإلكتروني

Mona maghraby

جامعة عين شمس

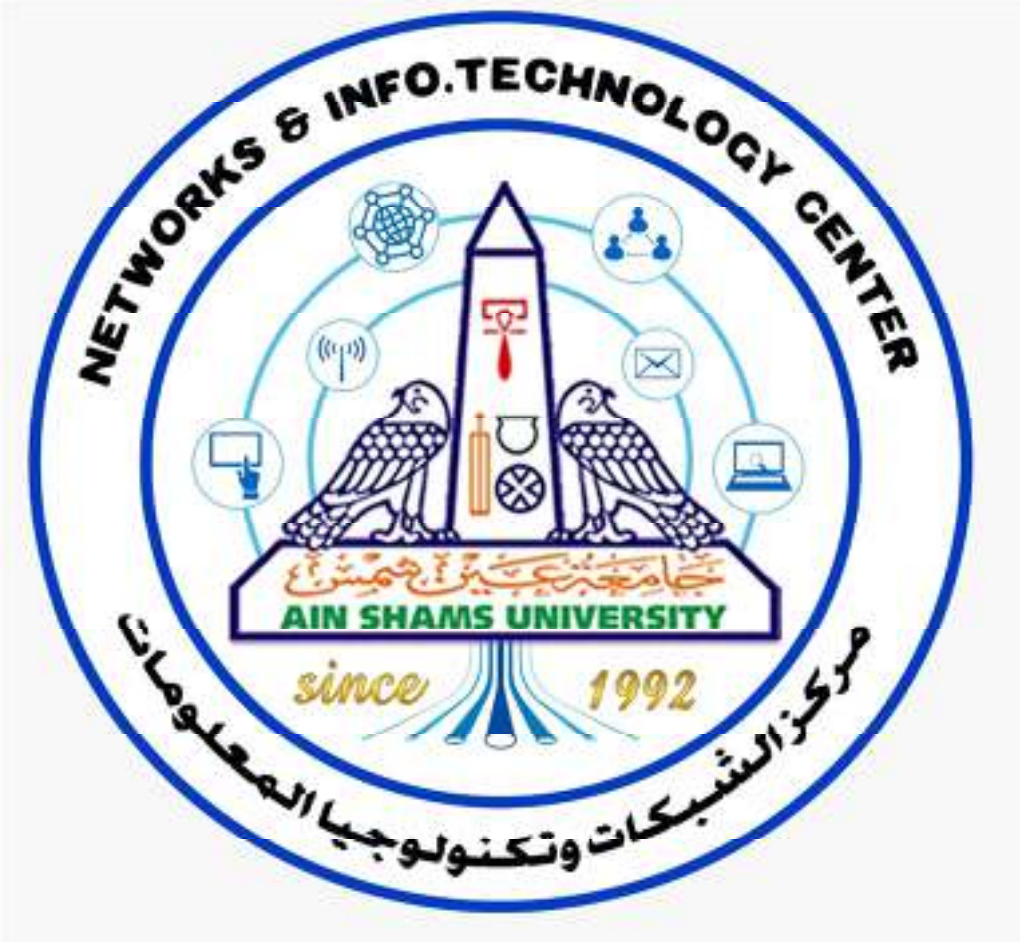
التوثيق الإلكتروني والميكروفيلم

قسم

نقسم باللّه العظيم أن المادة التي تم توثيقها وتسجيلها

علي هذه الأقراص المدمجة قد أعدت دون أية تغيرات

Mona maghraby



بعض الوثائق الأصلية تالفة
وبالرسالة صفحات لم ترد بالأصل

B1A.V.

Studies on some Ligands Containing Nitrogen ,Oxygen and Sulphur Donors and their Metal Complexes

A Thesis Submitted to
the Faculty of Science
Alexandria University

In Partial Fulfillment for the Requirements
for
Master Degree of Science in Chemistry

BY
Medhat Abdel Naiem Shaker
B.Sc. in Chemistry ,University of Alexandria ,1989

University of Alexandria
1996

SUPERVISORS

Prof. Dr. Mohamed A. Khalifa

Department of Chemistry

Faculty of Science

Alexandria University

Dr. Ismail Mahmoud Abid

Department of Physics & Chemistry

Faculty of Education (Damanhour)

Alexandria University

NOTE

Besides the work carried out in this thesis, the candidate ***Medhat Abdel Naiem Shaker*** has passed successfully the following courses in partial fulfilment of M.Sc. degree:

1. Inorganic Reaction Mechanisms.
2. Symmetry and Group Theory.
3. Instrumental Analysis.
4. Chemical Equilibria.
5. Electrochemistry.
6. Chemical Kinetics and Reaction Mechanism.
7. Thermodynamic in Solution.
8. Solid state chemistry.
9. Quantum chemistry.
10. Polymer chemistry.
11. Organic chemistry.
12. Physical Organic Chemistry.
13. German Language.
14. Elementary Course in teh basic

Prof. Dr. Laila M. Thabit

Head of th Chemistry Department

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To My Family

With all My Love

CONTENTS

Summary

SUMMARY

This thesis involves spectral studies on some ligands containing nitrogen, oxygen and sulphur donors, viz. *o*-phenylenediamine, *o*-aminophenol, *o*-aminothiophenol and some purine and pyrimidine derivatives. The electronic absorption spectra of these compounds have been measured in a wide variety of solvents which are selected to show wide variations in dielectric constant, refractive index and hydrogen bonding capacity. The aim was to quantitatively decompose the solvent spectral shifts into the different solute-solvent interactions. Several one-, two- and three-parameter equations have been used to correlate the spectral shifts with various emperical solvent polarity parameters using the multiple linear regression technique. The results of these calculations indicated that specific solute-solvent interaction in particular hydrogen bonding and non-specific interactions such as dispersion and dipolar effects provide a reasonable model for describing solvent induced spectral shifts in a predictive manner.

The effects of both time and temperature on the electronic spectra of some purine and pyrimidine derivatives were also studied in methanol, ethanol, and water at different temperatures. It was found that for the compounds which can form hydrogen bonding with the solvents, the absorbencies of these compounds at certain wavelengths change with time and temperature until constancies are reached. This was explained as a result of the formation of hydrogen bonded association complexes between these compounds and the solvents. Kinetic data as well as activation parameters are calculated for these changes.

Metal complexes of some of these ligands with some α-diketones (2,3-butanedione and benzil) were prepared and isolated by the template method These

complexes have been characterized via elemental analyses, magnetic moments, proton nuclear magnetic resonance, infrared and electronic studies. Two types of complexes were isolated square planar in case of Ni^{2+}, Co^{2+}, Cu^{2+} and Cd^{2+} ions, where the ligands act as dibasic tetradentate, and octahedral in case of Zn^{2+} ion, where the ligand in this case acts as neutral tetradentate with two acetyl groups occupy the axial positions of the complex.

Kinetic studies of the ligand substitution reactions of some six-coordinated Fe(II) complexes, $Fe(N_4)L_2$, were carried out spectrophotometerically in chloroform at four different temperatures. The reactions studied are in the form :

$$Fe(N_4)(L)_2+X \rightarrow Fe(N_4)(L)(X)+L$$
$$Fe(N_4)(L)(X)+X \rightarrow Fe(N_4)(X)_2+L$$

where L is N-methylimidazole; X is pyridine, 4-ethylpyridine, morpholine, dimethyl sulfoxide and tri-n-butylphosphite and (N_4) is the in-plane tetradentate macrocyclic ligands cyclohexanedienedioximato, $(CHDH)_2$, or dimethylglyoximato, $(DMGH)_2$.

These reactions were found to proceed through the formation of a five-coordinate intermediate that possesses little or no discriminating ability towards the entering nucleophiles. The rate data were thus interpreted in terms of a dissociative, D, or dissociative interchange, I_d, mechanism.. The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$were calculated from the application of the transition state equation to the temperature dependencies of the rate constants.

LIST OF FIGURES