PHYSIOCHEMICAL STUDIES ON COMPLEXES OF 2-ACETYL PHENYL AZO-β-DIKETONE LIGANDS WITH SOME TRANSITION AND LANTHANIDE IONS.

A THESIS

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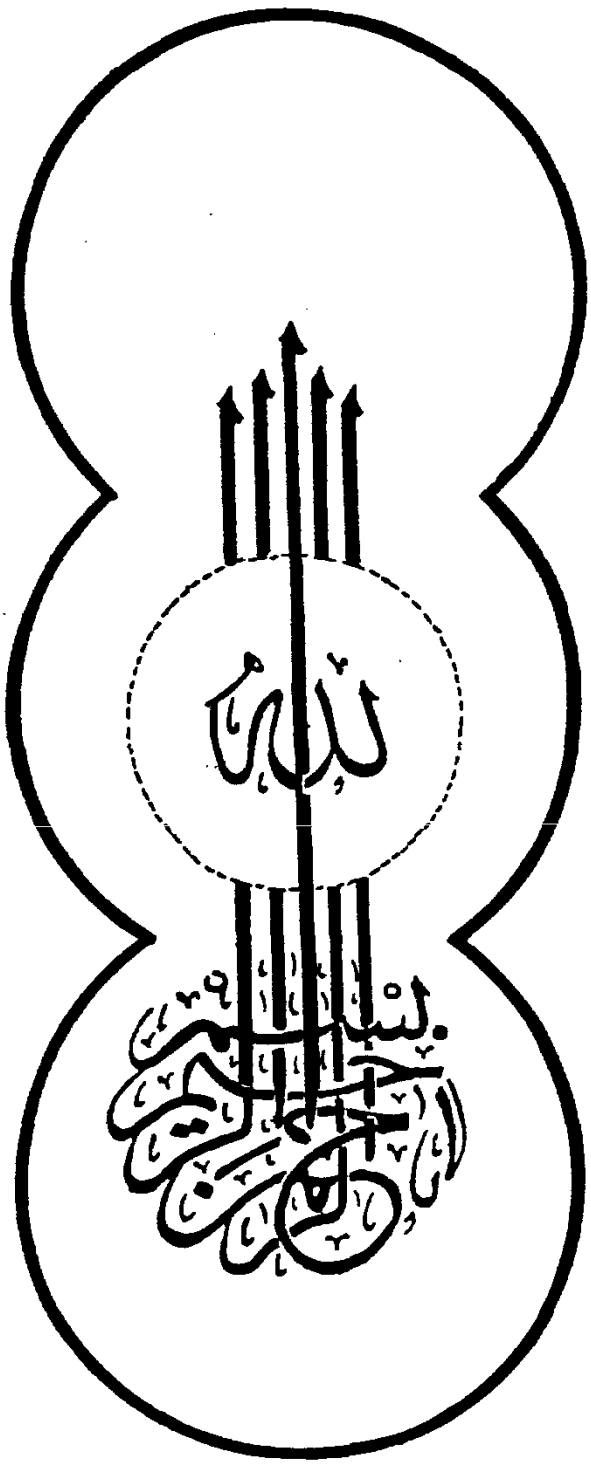

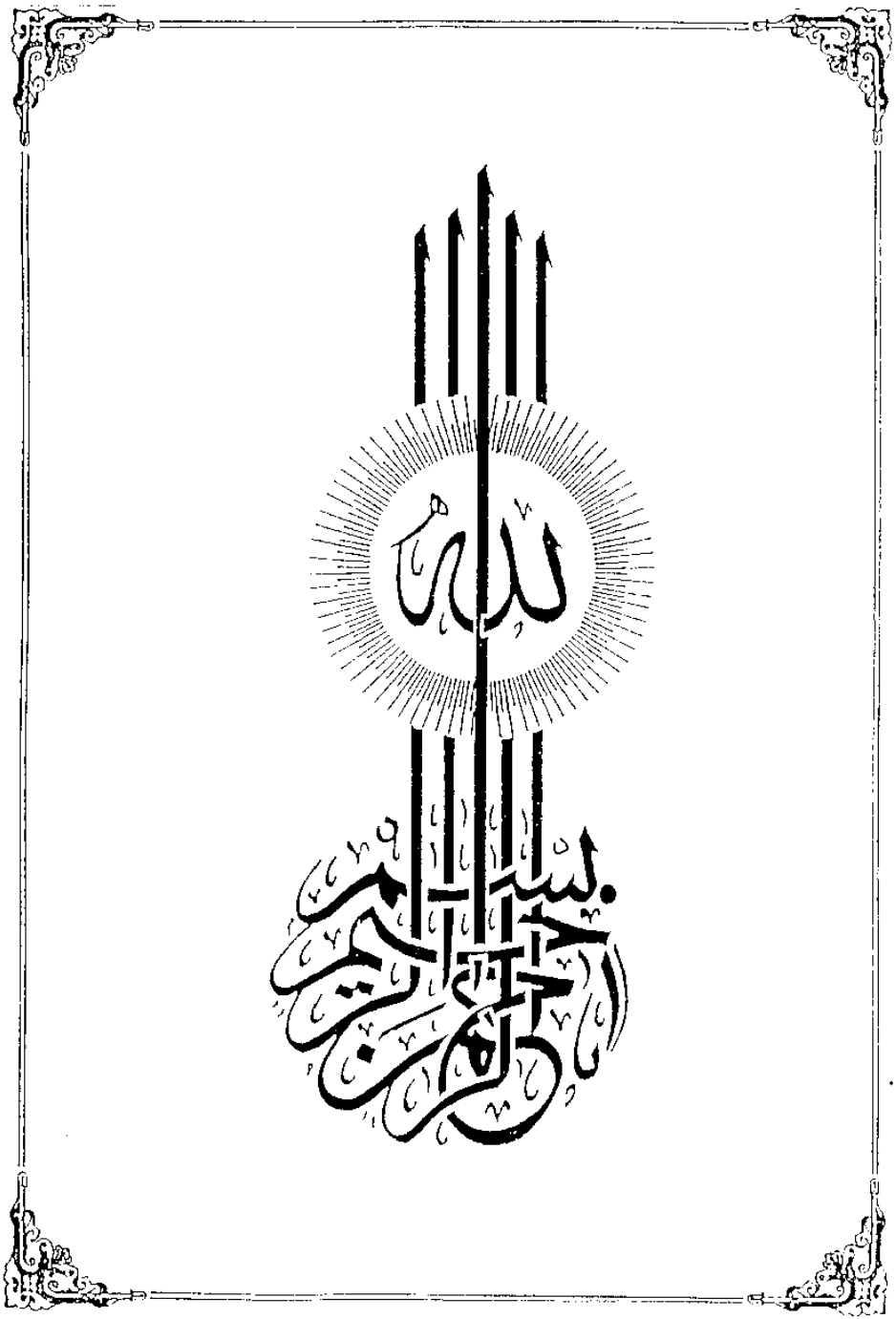

PHYSICOCHEMICAL STUDIES ON COMPLEXES OF

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SOME TRANSITION AND LANTHANIDE IONS.

THESIS ADVISORS

Prof. Dr. B. A. El-Shetary

Assist. Prof. Dr. M. S. Abdel-Moez

Dr. S. L. Stefan

APPROVED

Bashir EL-Shetary

M. S. Abdel-Moez

S. L. Stefan

Prof. Dr. N. GUINDY

Head of Chemistry Department

NOTE

Beside the work carried out in this thesis, the canadidate had attended graduate courses for one year in inorganic chemistry, covering the following topics :

1. Advanced Electrochemistry.
2. Solvent Extraction.
3. Chromatography.
4. Nuclear chemistry.
5. Inorganic Reaction Mechanism.
6. Instrumental Analysis.
7. Quantum chemistry & Spectroscopic application of group theory.
8. Organometallic compounds.
9. Computer.

He has successfully passed a written examination in these courses.

Prof. Dr. N. GUINDY

Head of Chemistry Dept.

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TO MY FAMILY

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AIM OF THE WORK

β -dikentones as well as hydrazone compounds were used widely as chelating agents with both transition and lanthanide elements. However, the combination product between the two classes of chelating agents form a new interesting compounds, which act as very good bi- or tri- dentate ligands.

The aim of the present work is the preparation of five related organic ligands by coupling diazonium salt of 2-aminoacetophenone with different β -diketones as acetylacetone, benzoylacetone, dibenzoylmethane, trifluoroacetylacetone and dimedone. The physicochemical properties of these ligands were studied to illustrate the effect of different structures in the β-diketone branch. This study includes complexation between different organic ligands and both transition metal ions & the tervalent lanthanide elements.

The composition and stability of complexes have been determined by pH-metric and spectrophotometric methods of analysis. The polarographic behaviour of some organic ligands as well as Cu^{2+}-ligand mixtures were studied at different pH's in universal buffer solutions , unbuffered solutions and in 40% dioxane-water(V V) solution. Also these chelating agents were used for determination of the concentration of copper ion in solution spectrophotometrically.

Due to the great importance of the azo compounds and their metal complexes which are used as pigments, paints, stabilizers of polymers and other coloured materials, the research program is directed to prepare and study the solid complexes between the organic ligands and transition metal ions. The elemental analysis and different physicochemical studies, as infrared, U.V., and visible spectra, molar conductance and magnetic properties, were performed on the prepared solid complexes.

CHAPTER I

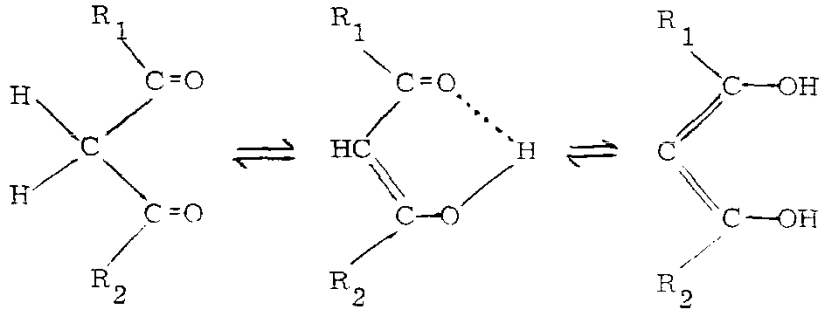
INTRODUCTION

INTRODUCTION

(i) Literature Survey on β-diketones and their properties :

The β-diketones were used as ligand and the chemistry of these compounds has aroused much recent interest in such diverse areas as spectral studies, gas chromatography, solvent extractions, column and thin-layer chromatography, NMR shift reagents, Laser technology and polymer industry[1-4].

The β-ketones can be described by the following tautomeric structures :-



β-diketone form β-enol form β-dienol form

Most of the β-diketones are usually mixtures of diketone and β-enol forms. Their keto-enol tautomerism is responsible for the formation of inner complex compounds with metals.

On the basis of classic bromoteric titrations[5-8] and recently by spectral methods, it was found that acetylacetone exists as an equilibrium mixture of keto and enol forms, containing 76-80%