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بسم الله الرحمن الرحيم

STUDIES ON SOME AMINO ACID DERIVATIVES AND THEIR COMPLEXES

A Thesis

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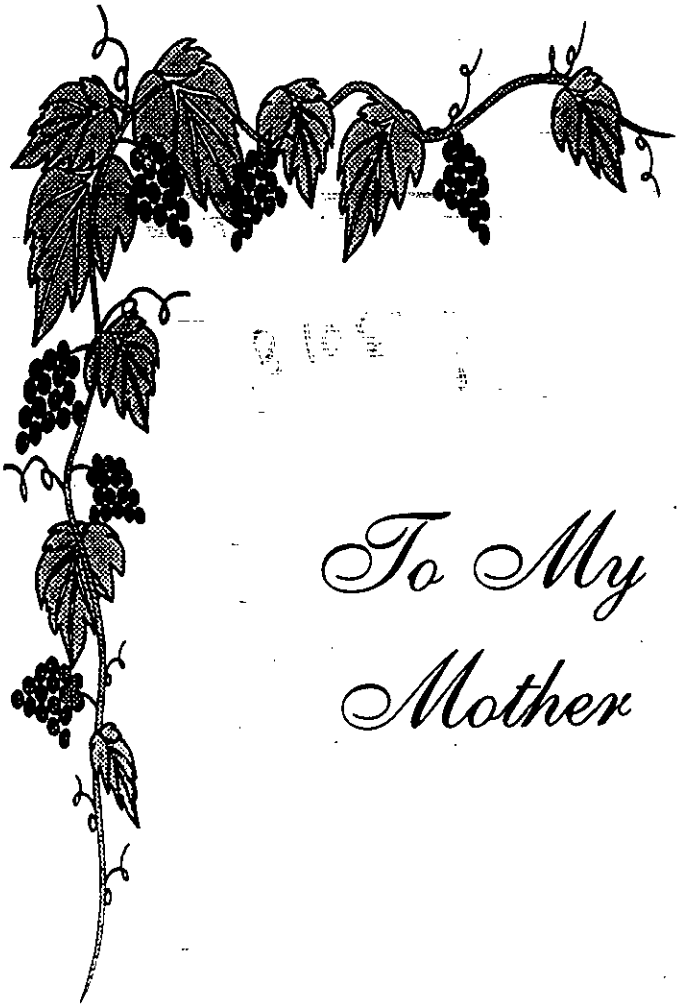

To My
Mother

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SUMMARY

The thesis comprises three chapters. The first concerns with the literature survey on the biological importance and coordiantion properties of some amino acids especially N-protected glycine, phenylalanine and proline.

The second chapter deals with the experimental methods. The synthesis of the ligands (N-carbobenzyloxyglycine, N-carbobenzyloxy-L-phenylalanine and N-carbobenzyloxy-L-proline) and their metal(II) chelates with some transition elements (Co(II), Ni(II), Cu(II), Pd(II) and Pt(II)) is described.

The analytical data and the different instruments utilized for the measurements in these studies (^{1}H NMR, IR, UV-Vis, mass spectra, ESR and magnetic susceptibility) are also described. Potentiometric titrations using the glass-Ag/AgCl electrode system were employed for determing the protonation constants of the ligands and the stability constants of their metal(II) chelates, as it is the most accurate and reliable technique. The careful methods and all the necessary precautions, particularly the calibration of the potentiometric system, are described. This chapter deals also with the experimental methods used for the purification of the nitrogen gas, the solvents, the potassium hydroxide and other chemicals, and the preparation and standardization of the solutions used.

The third chapter presents the results obtained in this work and discusses their interpretation. The ^{1}H-NMR spectra of the prepared ligands proved that they exist in the carboxy-imino form and that there is no exchange of the imino proton with the adjacent groups.

The mass spectral studies of the ligands and their metal(II) chelates are then discussed. All the ligands under investigation gave peaks corresponding to their molecular ions. Two major fragmentation pathways are followed by the molecular ion of N-carbobenzyloxyglycine. The first one includes the rupture of both bonds β to nitrogen with subsequent cyclization. The base peak is produced from this rupture and it is assigned as benzyl alcohol. The second fragmentation pathway includes the rupture of the bond β to the aromatic ring to give a resonance stabilized benzyl ion which rearranged to the highly stable tropyllium ion. The base peak in the spectrum of N-carbobenzyloxy-L-phenylalanine is produced by the rupture of C-C bond β to the carboxylic group to afford the tropyllium ion at m/e 91. The driving force for such cleavage was attributed to both resonance stabilization and steric factors. In case of N-carbobenzyloxy-L-proline, the base peak is produced by the cleavage of the pyrrolidine ring. Most of the complexes did not give their molecular ion peaks but they gave some metal containing fragments. This was attributed to the ease of decomposition on electron impact or the high degree of polymerization.

Potentiometric titrations are used to study the solution equilibria of the ligands both alone and in presence of cobalt(II), nickel(II) or copper(II) ions. The medium used was 50% (v/v) ethanol-water at 30.0°C, and at ionic strength of 0.05 M potassium chloride. The titration curves were analysed using the SUPERQUAD program. Each ligand has only one protonation constant which refers to the protonation of the carboxylate group. No evidence for the protonation of a second site (the imino group) in any of the three ligands was observed, in spite of attempting titrations in presence of adequate amounts of added hydrochloric acid. This is because the peptide type linkage is not easily protonated. It was found that the stabilities of cobalt(II), nickel(II) and copper(II) complexes follow the Irving-Williams series. The pK_W for water in this medium was found to be 14.374 ± 0.008.

The electronic spectra and magnetic susceptibility measurements were used to demonstrate the stereochemistries of the prepared metal(II) chelates. All the cobalt(II) chelates have high-spin octahedral spatial configuration while all the nickel(II) chelates have tetrahedral geometry.

The polycrystalline ESR spectra of the copper(II) complexes at room temperature were also discussed in this chapter. The data