

بسم الله الرحمن الرحيم





شبكة المعلومات الجامعية التوثيق الالكتروني والميكروفيلم



جامعة عين شمس

التوثيق الإلكتروني والميكروفيلم

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B1VCC

PHYSICO CHEMICAL STUDIES ON METAL COMPLEXES OF SOME THIOSEMICARBAZIDE AND SEMICARBAZIDE LIGANDS

A THESIS

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for

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By

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- 2- Coordination Chemistry.
- 3- Advanced Analytical Chemistry.
- 4- Group Theory.
- 5- Solid State Chemistry.
- 6- Electro-Chemistry.
- 7- Quantum Chemistry.
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AIM OF WORK

Metal complexes of thiosemicarbazides and semicarbazides are of current interest due to their biological activity against smallpox, viral diseases and certain types of tumours. In this thesis, copper (II) complexes of 4-phenyl-1-aryl-3-thiosemicarbazide (H_2L^1 , H_2L^3 and H_2L^5) and 4-phenyl-1-aryl-3-semicarbazide (H_2L^2 and H_2L^4) have been prepared and characterized using analytical, spectral and magnetic techniques in order to understand fully the diverse coordinating properties and reactivity of this important class of ligands.

SUMMARY

SUMMARY

The thesis divided into three main chapters:

I-Introduction :

In this chapter, a literature survey is made on the following:

1-1. The importance of thiosemicarbazides and their metal complexes.

1-2.-Metal complexes of 4-phenyl-1-aroyl-3-thiosemicarbazides.

II- Experimental:

In this chapter, the methods used for the preparation of thiosemicarbazides, semicarbazides and their Cu(II) complexes were described. The techniques for the analytical, spectral (I.R., U.V. and visible), electron spin resonance (E.S.R.) and magnetic susceptibility measurements were also discussed.

III- Results and Discussion:

In this chapter complexes of Cu(II) with derivatives of 4-phenyl-1-aroyl-3-thiosemicarbazide (H_2L^1 , H_2L^3 and H_2L^5) and 4-phenyl-1-aroyl-3-semicarbazide (H_2L^2 and H_2L^4) have been described. The complexes have been studied using analytical, spectral (I.R., U.V, visible and E.S.R) and magnetic measurements. The analytical, magnetic and spectral studies show that the ligands react with different salts of copper(II) ions in 1:1 molar ratio forming different types of complexes. Complexes of the type $Cu (H_2L)_2X_2$, $X = Cl, Br, O\bar{A}c$, $L = L^2, L^4$ and

L^5 produced, in this type of complexes the ligands behave as a neutral bidentate ligands and coordination takes place via the thion sulphur atom or carbonyl oxygen and $\overset{1}{N}H$ group. The ligands can also behave as mononegative bidentate ligands as in the case of $Cu(HL)_2$, $L = L^1, L^2$ and L^4 . The ligands coordinating through the thiol sulphur or enol oxygen and $\overset{1}{N}H$ group. Third type of complexes also obtained in which the ligands behave as mononegative tetradentate ligands as in the case of $CuHLX(H_2O)$ where $L = L^1, L^2$ and L^5 , $X = NO_3, Br$ and Cl . In these complexes the ligands coordinate via the thiol sulphur or enol oxygen and $\overset{1}{N}H$ group from one end and a carbonyl oxygen and azomethine nitrogen from the other end, to form polymers.

A fourth type of complexes have been produced in which the ligands behave as dinegative tetradentate, coordinating through the thiol sulphur or enol oxygen and $\overset{1}{N}H$ group as $(C=N)$ from one end and the enolic oxygen and $\overset{2}{N}H$ group as $(C=N)$ from the other end forming polymeric complexes as shown in scheme 3.

Finally, complexes of the type $CuH_2LHLX(H_2O)$ have also obtained. In this complexes H_2L behaves as neutral bidentate and HL behaves as monovalent bidentate. The magnetic susceptibility measurements, electronic spectra and E.S.R. spectra reveal that the complexes display octahedral geometries except, $Cu(HL^1)_2$, CuL^1 , $Cu(HL^2)_2$, $Cu_2HL^3Cl_3(H_2O)$, CuL^3 and CuL^4 exhibit square planar geometries.

CHAPTER I INTRODUCTION

CHAPTER [I]

INTRODUCTION

1-1. Importance of complexes:-

Metal complexes of thiosemicarbazides and thiosemicarbazones, semicarbazides and semicarbazones have recently attracted special attention due to their biological activity against smallpox, viral diseases and certain types of tumours⁽¹⁻²⁾. Aromatic thiosemicarbazide derivatives and their complexes⁽³⁻⁷⁾ are of interest for their biological applications as drugs, but since their toxicity is very strong⁽⁸⁾, novel derivatives are being sought in an attempt to find new uses⁽⁸⁻¹¹⁾. Metal complexes of thiosemicarbazide have also drawn special attention due to their pharmacological, anti-bacterial, fungicidal properties⁽¹²⁻¹⁴⁾ and have also been recorded as agricultural fungicides. Growth inhibition of *Aspergillus terreus* and antifungal activity against human pathogens⁽¹⁵⁾. Substituted thiosemicarbazides and their corresponding cyclized 1,3,4-oxadiazoles⁽²⁷⁾ used as anti-inflammatory drugs and possess antiproteolytic activity⁽¹⁶⁻¹⁸⁾.

The anti-inflammatory activity was determined by the ability of these agents to provide protection against carrageenin-induced edema in rat paw, and their ability to inhibit trypsin-induced hydrolysis of bovine serum albumin reflected the antiproteolytic activity possessed by these compounds.