CONTENTS

Summary

The present thesis comprises three main chapters

Chapter I (Introduction):-

In this chapter, a literature survey was given on the followig topics:

1- The chemical and biochemical importance of copper (II) ion and its complexes.

2- The chemical and biochemical importance of Schiff base metal complexes.

3- The chemical and biochemical importance of pyrrole derivatives.

4- Thermal analysis and its application on metal complexes.

5- Background about entomopathogenic nematodes *(Steinernema carpocapsae and Heterorhabditis bacteriophora)*
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6- Background about *Galleria mellonella*, including taxonomy of the insect and short notes about the family Pyralidae.

Chapter II (Experimental):-

This chapter includes a detailed account about the methods of preparing ligands and their copper (II) chelates. The experimental techniques used were described and the sources of *G. mellonella* and nematode species (*Steinernema carpocapsae* and *Heterorhabditis bacteriophora*) were mentioned.

Chapter III (Results and Discussion):-

This chapter includes the results obtained and their discussions, this chapter comprises five main parts:

Summary

Part I

In this part, the Schiff base ligand (HL^1) derived from 2-amino-3-cyano-1,5-diphenylpyrrole and salicylaldehyde and its copper (II) complexes have been prepared and their structures were investigated by different analytical and spectral methods. The thermal behavior and the decomposition pathways of the complexes obtained have also been studied, the analytical and spectral data of the investigated ligand confirm its structure. The careful investigation shows that, these complexes are characterized by:-

1- They are air stable, non- hygroscopic, non electrolytes, soluble in methanol and/or acetonitrile and are insoluble in most common organic solvents, freely soluble in the coordinating solvents as DMF or DMSO.

2- According to analytical data, complexes (**1, 2, 4**) show 1M:1L molar ratio while complex (**3**) shows 1M:3L molar ratio.

3- From both UV-vis and electron paramagnetic resonance (EPR) spectra, complexes (**1, 2** and **4**) have square planar geometry while the complex (**3**) has octahedral geometry.

4- The higher value of magnetic moment (1.9-2.0 BM) than the spin only value (1.73 BM) may be due to orbital angular momentum contribution in d^9-system, corresponding to one unpaired electron. These values indicate absence of spin-spin interaction, this behavior is mainly attributed the complexes present in monomeric structures.

5- Thermal analysis data show that, complexes (**1, 2** and **4**) have lower thermal stability (100-151 ^{0}C) than complex (**3**); this behavior may be due to the presence of these complexes in ketoamine-enolimine toutomeric forms. For complex (**3**) the higher thermal stability (310 ^{0}C) may be due to presence of three six membered chelates rings around Cu (II) ion.

6- For complex (**2**) the solvent of crystallization have different nature of the interaction in the lattice.

7- The counter ligands (Cl^-, NO_3^-, OAc^-, Br^-) play a significant role on the nature of decomposition pathways as well as the final products.

Part II

In this part, the Schiff base ligand (HL^2) derived from 2-amino-3-cyano-1,5-diphenylpyrrole and 2-hydroxy-1-naphthaldehyde and its copper (II) complexes have been prepared, their structures were investigated by different analytical and spectral methods. The thermal behavior and the decomposition pathways of the complexes obtained have also been studied, the analytical and spectral data of the investigated ligand confirm its structure. The careful investigation shows that, these complexes are characterized by:-

1- They are air stable, non- hygroscopic, nonelectrolytes, soluble in acetonitrile and insoluble in most common organic solvents, freely soluble in the coordinating solvents as DMF or DMSO.

2- According to analytical data, complexes (**5-7**) present in 1M:2L molar ratio, while complex (**8**) presents in 1M:1L molar ratio.

3- From both UV-vis and electron paramagnetic resonance (EPR) spectra, complexes (**5, 8**) have square planar geometry, while complexes (**6, 7**) have square pyramidal geometry.

4- The higher value of magnetic moment (1.8-2.0 BM) than the spin only value (1.73 BM) may be due to orbital angular momentum contribution in d^9-system, corresponding to one unpaired electron. These values indicate the absence of spin-spin interaction.

5- Thermal analysis data show that, complexes (**5-7**) have higher thermal stability (270- 331 ^{0}C) than complex (**8**) their higher thermal stability may be due to the presence of two six membered chelates rings around Cu(II) ion. The lower thermal stability (150 ^{0}C) of complex (**8**) may be due to its presence in ketoamine-enolimine toutomeric form.

6- The counter ligands (Cl^-, NO_3^-, OAc^-, Br^-) play a significant role on the nature of decomposition pathways as well as the final products.

Part III

In this part, the Schiff base ligand (L^3) derived from 2-amino-3-cyano-1,5-diphenylpyrrole and thiophene-2-carboxyaldehyde and its copper (II) complexes have been prepared and their structures were investigated by different analytical and spectral methods. The thermal behavior and the decomposition pathways of the complexes obtained have also been studied, the analytical and spectral data of the investigated ligand confirm its structure. The careful investigation shows that, these complexes are characterized by:-

1- They are air stable, non- hygroscopic, soluble in acetonitrile and/or methanol, are insoluble in most common organic solvents and freely soluble in the coordinating solvents as DMF or DMSO.

2- According to analytical data, complexes (**9, 10**) show 1M:1L molar ratio, while complex (**11**) shows 1M:2L molar ratio and complex (**12**) shows dimmeric structure.

3- Complexes (**9, 10**) show 1:1 electrolytic nature, complex (**11**) is non electrolyte and complex (**12**) is 1:1 electrolyte.

4- From both UV-vis and electron paramagnetic resonance (EPR) spectra, complex (**9**) has square planar geometry, complexes (**10, 11**) have octahedral geometry and complex (**12**) has distorted tetrahedral geometry.

5- The higher value of magnetic moment of complexes (**9-11**) (1.9-2.0 BM) more than the spin only value (1.73 BM) may be due to orbital angular momentum contribution in d^9-system, corresponding to one unpaired electron. These values indicate the absence of spin-spin interaction. Complex (**12**) shows low value of magnetic moment (1.1 BM) which is lower than the spin only value, indicating the presence of spin-spin interaction.

6- Thermal analysis data show that, complexes (**9, 10**) have relatively lower thermal stability (111-136 ^{0}C) than complexes (**11**, **12**) which show thermal stability 146 and 169 ^{0}C, respectively.

7- For complexes (**9, 10**) the solvent of crystallization have different nature of the interaction in the lattice.

8- The counter ligands (Cl^-, NO_3^-, OAc^-, Br^-) play a significant role on the nature of decomposition path ways as well as the final products.

Part IV

In this part, the Schiff base ligand (H_2L^4) derived from 2-amino-3-cyano-1,5-diphenylpyrrole and 2,4-dihydroxybenzaldehyde and its copper (II) complexes have been prepared and their structures were investigated by different analytical and spectral methods. The thermal behavior and the decomposition pathways of the complexes obtained have also been studied, the analytical and spectral data of the investigated ligand confirm its structure. The careful investigation shows that, these complexes are characterized by:-

1- They are air stable, non- hygroscopic, soluble in methanol and insoluble in most common organic solvents, freely soluble in the coordinating solvents as DMF or DMSO.

2- According to analytical data, all complexes (**13-16**) show 1M:1L molar ratio.

3- Complexes (**13, 14 and 16**) show 1:1 electrolytic nature, while complex (**15**) is nonelectrolyte, the higher molar conductivity value for complex (**14**) may be due to partial replacement of the coordinated nitrate anion by DMF molecules.

4- From both UV-vis and electron paramagnetic resonance (EPR) spectra, complexes (**13-15**) have octahedral stereochemistry while complex (**16**) has distorted tetrahedral geometry.

5- The higher value of magnetic moment (1.9-2.0 BM) than the spin only value (1.73 BM) may be due to orbital angular momentum contribution in d^9-system, corresponding to one unpaired electron. These values indicate the absence of spin-spin interaction.

6- Spectral and thermal data indicate that, complexes (**13-15**) behave similarity.

7- The counter ligands (Cl^-, NO_3-, OAc^-, Br^-) play a significant role on the nature of decomposition pathways as well as the final products.

i) Solvent of crystallization (ethanol) is physically bound in all bromide copper (II) complexes (**8, 12, 16**) except complex (**4**).

ii) For all the investigated complexes the kinetic and thermodynamic parameters (E^*, ΔS^*, ΔH^*, ΔG^*) have been calculated.

Part V

Biological activity

This part includes the obtained results on biological activity and their discussions and contains the following topics:-

Summary

1- Mortality test.

For *H. bacteriophora* at 48h, the mortality of the nematodes increased with increasing concentrations of copper (II) ion, ligands and complexes. Insignificant increase in mortality was occurred from the median to the high concentration. At the low concentration, Cu (II) ion appeared to be the most toxic for the nematode juveniles while complexes (**1, 9**) have no toxicity. At the high dose, Cu (II) ion also scored the highest toxicity followed by HL^2, H_2L^4, HL^1, L^3, complex **(5)**, complex (**13**), complex **(1**) then complex (**9**). The values of the percentage mortality of the juveniles were increased at 96h exposure to Cu(II) ion, ligands and complexes with the same rank of 48h.

For *Steinernema carpocapsae* at 48h, Cu (II) ion was the only toxic for the juveniles at the low concentration. This toxicity increased with increasing concentrations. The mortality appeared at the median concentration in the rank HL^2, HL^1, H_2L^4 and L^3. All the tested complexes have no effect on it. The same rank of mortality at 48h was occurred at 96h with increasing the values of percentage mortality of the nematode juveniles.

2- infectivity test.

The infectivity of Cu (II) ion treated *H. bacteriophora* and *S. carpocapsae* juveniles (low and high concentrations) was generally reduced as compared with that of control (33.30 % and 11.50 %) and (88 % and 75 %) respectively. The infectivity of the ligands and complexes treated *H. bacteriophora* and *S. carpocapsae* juveniles with low and high concentrations matches that of the non-treated nematodes (100%).

3- Rate of reproduction.

The reproduction of *H. bacteriophora* and *S. carpocapsae* decreased with increasing concentrations of copper(II) ion, ligands and complexes. At high concentration of *H. bacteriophora* the rank of the reproduction potential was as follows: complex **(9),** complex **(13),** complex (**5**), complex **(1)**, L^3, H_2L^4, HL^2, HL^1 and finally Cu (II) ion. At low concentrations, the rank was the same where complex (**9**) was the one that scored the highest reproduction potential (85492.81 IJs\L) followed by complex (**13**), complex (**5**), complex (**1**), L^3, H_2L^4, HL^1, HL^2 and Cu (II). For *S. carpocapsae,* at high concentrations, the rank of the reproduction potential was as follow: complex (**9**), complex (**5**), complex (**13**), complex (**1**), L^3, HL^1, HL^2, H_2L^4 and finally Cu (II) ion. complex (**9**) shows reproduction potential (111296.76 IJs\L) more than control (97731.39 IJs\L). At low concentrations, the rank was the same, complex **(9**) still the one that scored the highest reproduction potential (112296.76 IJs\L). The explanation of this result may that complex (**9**) makes activation for the infective stage juveniles and consequently enhance the nematode reproduction.

We can concluded that:-

i) For *H. bacteriophora,* L^3 and complex (**9**) are the least toxic and complex (**9**) scored the highest rate of reproduction.

ii) For *S. carpocapsa,* ligand (L^3) is also less toxic but all complexes have no effect. Complex (**9**) scored the highest reproduction potential over that of the control, the explanation of this result may be due to the that this complex makes activation for the infective stage juveniles in low and high concentration and consequently enhance the nematode reproduction, this effect may be due to the presence of thiophene moiety in the complex structure together with complexation effect.