SUMMARY

This thesis includes three chapters; the introduction, experimental and results and discussions.

- CHAPTER (1)

In this chapter, a literature survey of the pervious studies carried out on macrocyclic compounds and their complexes with transition metal ions is given. This survey includes electronic absorption spectra in the UV and visible regions, studies on the metal chelates formed with different transition metal ions, the different techniques of structure elucidation of metal macrocyclic complexes.

- CHAPTER (2)

This chapter describes the experimental part where it includes the preparation of the Fe(III), Co(II), Ni(II) and Cu(II) macrocyclic complexes by template reaction. It comprises also a description of the instruments used for spectrophotometric, conductometric, IR, thermal analysis, electron spin resonance spectroscopy of Cu(II) complexes, x-ray diffraction, scanning electron microscope, magnetic susceptibility measurements, catalytic studies and electrical conductivity measurements.

- CHAPTER (3)

This chapter includes the results and discussions and it comprises to three main parts:

A- Structure elucidation of the prepared macrocyclic complexes:

The structures of the solid complexes were firstly confirmed by elemental analysis of the isolated chelates. Data of elemental analysis show satisfactory agreement with the proposed formula. All the solid complexes are soluble in DMF but insoluble in common organic solvents and do not posses sharp melting points but decompose on heating above 530 °C. The molar conductivities of the complexes in DMF indicate that all of the complexes are of ionic nature.

The results of thermal analysis of some selected solid macrocyclic complexes show that they degrade in three stages. The first step in the decomposition sequence corresponds to the loss of physically combined water molecules from the outer surface or interstice of the crystal lattice. The second step within the temperature range 140 – 530 °C represent the thermal decomposition of the CH_3 and CH_2 groups support the proposed structure. The CH_3 groups start to decompose at 140°C followed by CH_2 groups and the compensation of nitrogen atoms to give N_2 gas. The latter decomposed in the final step forming CoO, NiO or CuO as a final product. The number of coordinated water molecules and the percent of metal ions were calculated from the weight loss on the TG curves whose values are in good agreement with those obtained from elemental analysis.

Magnetic susceptibility measurements were carried out at room temperature using Gouy's balance method. The $\mu_{eff.}$ values of the selected complexes show normal values for distorted octahedral complexes.

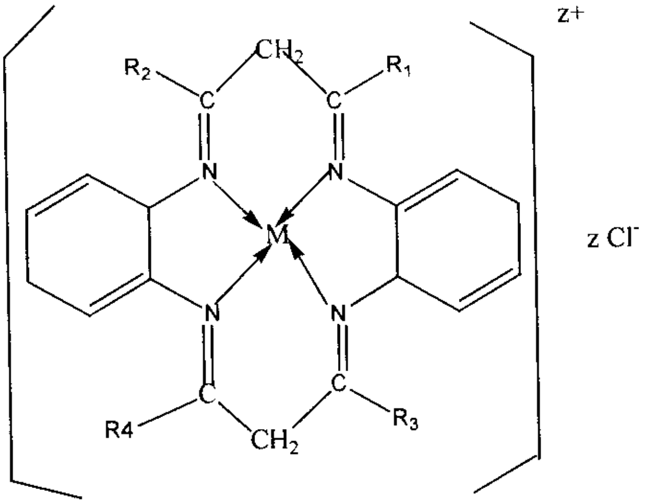
Further support of the mode of bonding taking place in the solid complexes was obtained by IR spectroscopy. The IR absorption spectra of the solid macrocyclic complexes with ligand molecules based on diphenylamine and diketones. IR spectra of macrocyclic complexes formed between o-phenylene-diamine and p-phenylene-diamine with acetylacetone, benzoylacetone and dibenzoylmethane.

The IR spectrum of o-phenylenediamine and p-phenylenediamine show broad bands at 3362-3373 cm^{-1} which are due to the stretching vibrational mode of the NH_2 groups and the strong band at 1596-1655 cm^{-1} due to the stretching vibration of the C=O expected to present in the diketone molecule. The IR spectra of Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} complexes show the absence of the first two bands with the appearance of new sets of bands at 1602-1657 cm^{-1}due to the stretching vibration of the C=N group ($\upsilon_{sym.C=N}$) resulting from the condensation of C=O and NH_2 groups of the acetylacetone and o-phenylenediamine respectively in the template reaction. These bands are found at so lower frequencies due to the participation of the nitrogen atom of the azomethine group in the coordination bonds. The stretching vibration bands of the active methylene group (υ_{CH2}) of the diketone moiety suffer a shift toward lower frequency side as a result of electron delocalization due to complex formation. The metal to nitrogen bonds ($\upsilon_{M\text{-}N}$) give rise to a medium-strong bands at 370-461 cm^{-1} according to formation of macrocyclic complexes.

The electronic absorption spectra of Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} macro complexes were scanned in the UV-visible range in solution using DMF as solvent and in solid state using Nujol mull technique. The spectra show bands due to π-π^* transitions within the ligand (UV region), M → L or L → M transitions and d-d transitions in far visible region.

The electronic spectra of the majority of Fe^{3+} macro complexes show two broad bands and a shoulder within the ranges 13552-19205 cm^{-1}, 17637-19841 cm^{-1} and 22026-26666 cm^{-1} corresponding to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4A_{1g}$ transitions in octahedral field. On the other hand, spectra of Co^{2+} macro complexes are characterized by two broad bands within the ranges 15026-51097 cm^{-1} and

19712-23697 cm^{-1} corresponding to $^4T_{1g} \rightarrow ^4A_{2g}$ and $^4T_{1g} \rightarrow ^4T_{1g}(P)$ transitions, respectively. This indicates an octahedral environment around the Co^{2+} ions. All the investigated Ni^{2+} complexes show diamagnetic behavior except those of o-phenylenediamine with acetylactone and dibenzoylmethane which showed paramagnetic character. The electronic spectra of the other two Ni^{2+} macro complexes show two broad bands within the ranges 15198-22963 cm^{-1} and 21032-24752 cm^{-1} assignable to the $^3A_{2g} \rightarrow ^3T_{1g}$ (F) and $^3A_{2g} \rightarrow ^3T_{1g}$ (P) transitions, respectively in octahedral field. The electronic spectra of Cu(II) complexes show two broad band within 13774-20284 cm^{-1} and 16103-21459 cm^{-1} which can be assigned, respectively to $^2E_{2g} \rightarrow ^2B_{1g}$ and $^2A_{1g} \rightarrow ^2B_{1g}$ transition in a tetragonally distorted octahedral configuration.



1- $R_1=R_2=R_3=R_4=CH_3$
2- $R_1=R_3=CH_3$, $R_2=R_4=Ph$
3- $R_1=R_2=R_3=R_4=Ph$
M = Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}

The room temperature of ESR spectra of macrocyclic Cu (II) complexes with o-phynelenediamine-acetylacetone, p-phynelenediamine-acetylacetone and p-phynelenediamine - dibenzoylmethane showed anisotropic spectra with $g_{\parallel} > g_{\perp}$ characteristic for distorted elongated tetragonal copper (II) complexes with $d_{x^2-y^2}$ ground state. The shifting of a g-value from 2.0023 in transition metal complexes is due to the mixing via spin-orbit coupling of the metal orbitals involved in molecular orbitals containing the unpaired electron(s), with the empty or filled ligand orbitals. For Cu (II) complexes, the $g_{||}$ value is a sensitive parameter to indicate degree of covalency. For a covalent complex, $g_{||} = 2.3$ or more. The polycrystalline x-band ESR spectra of Cu(II) macrocyclic complex with o-phynelendiamine and dibenzoylmethane show anisotropic nature characteristic of tetragonal compressed with d_{z^2} ground state and $g_{\perp}$ value > $g_{||}$. The value of transition energy ($E_{dz^2} - E_{dxy,dxz}$) corresponding to $B_{1g} \rightarrow {}^2E_g$ was calculated. Deviation in the g value of this complex from 2.0023 of free electron is due to the covalence property as gathered from the G value which indicated to the interaction in the solid complexes. ESR spectra of Cu(II) complexes with benzoylacetone, o-phynelenediamine and p-phynlenediamine are show splited giving rise to three g value. The weak and broad signals are due to the polymeric nature of these complexes. The broad signal is common in many copper complexes and is attributed to the dipolar broadening enhanced spin-lattice relaxation property.

The X-Ray diffraction has been made for the Co^{2+}(o-phenylenediamine-acetylacetone), Co^{2+}(o-phenylenediamine-benzoylacetone), Cu^{2+}(o-phenylenediamine-acetylacetone) and Ni^{2+}(o-phenylenediamine-acetyl-acetone) macrocomplexes. All the prepared complexes show a peaks at 2θ about 5.5-15.7 Å that indicate the presence of layer structure and show the absence of a single phase structure.

Scanning electron microscope for Cu^{2+} (o-phenylenediamine-acetyl acetone) macrocyclic complex. The micrograph shows a species of different size ranging from 50 μm up to 150 μm. the perfect shape of the particles give an indication that the prepared materials are composed of multiphase as represented from the XRD. It is also seemed to have layer structure.

B- Kinetic studies on the oxidation process of catechol by Fe(III), Co(II), Ni(II) and Cu(II) complexes:

In this part, the kinetic of catalytic oxidation of catechol by Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} macro complexes to the corresponding o-benzoquinone were studied at different concentrations of catechol and catalyst (macro complex) was studied. The effect of time on the catalytic oxidation of catechol show that the absorbance corresponding to o-benzoquinone measured at 270 nm was increase by increasing the time. The catalytic activities of the macrocyclic complexes under study on the catechol oxidation were calculated. Under first order conditions, the rate of the reaction with Co(p-phenylenediamine-dibenzoylmethane) was much faster compared to Ni(o-phenylenediamine-dibenzoylmethane) due to an increased probability of an electron transfer.

C- Electrical conductivity of the solid state macrocyclic complexes:

The effect of a.c field on conduction process in macrocyclic complexes could be discussed in the basis of the selected macro cyclic complexes. This contains free ions and mobile (bounded in the network). Under the influence of the applied electric field, the free ions may migrate through the complex network. Their migration depends on the energy required to transfer ions from their interstitials site to another vacant site.

The activation energy for transportation of the ions depends on the charge of new site. An attractive or repulsive coulomb force between the ions and the site are established with considerable equality of the two

charges, which leads to very small energy values or a stability of conductivity with temperature.

The dielectric properties in the investigated complexes such as dielectric constant ε′, ε″ and tan δ arises from the dipole orientation in ionic material which changes according to the frequency of applied a.c field as well as the ambient temperature. The rise of a.c field accompanied by the decrease of ε′ ε″ and tan δ are due to the orientation of the dipole segments which arise from ionic diffusion of the ions through a certain barrier in this range of frequency. The rise in temperature may not facilitate the dipolar orientation in the complex, and may leads to structural relaxation with increasing temperature. Small peaks in ε′, ε″ and tan δ against temperature curves are attributed to some relaxation in the complex structure assisting to the dipolar orientation produced from pairs of electronic defects.