SUMMAY

SUMMARY

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

1- In the first chapter, a literature survey of the previous studies on monoazo and bisazo compounds along with 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 complexes and polarographic studies on the monoazo and bisazo compounds.

2- The experimental part (Chapter II) includes the preparation of the monoazo and bisazo compounds under investigation. It comprises also a description of the instruments used for spectrophotometric, conductometric, polarographic, IR, ^{1}H-NMR, thermal analysis and magnetic susceptibility measurements.

3- Chapter III includes the results and discussion it consists of three parts.

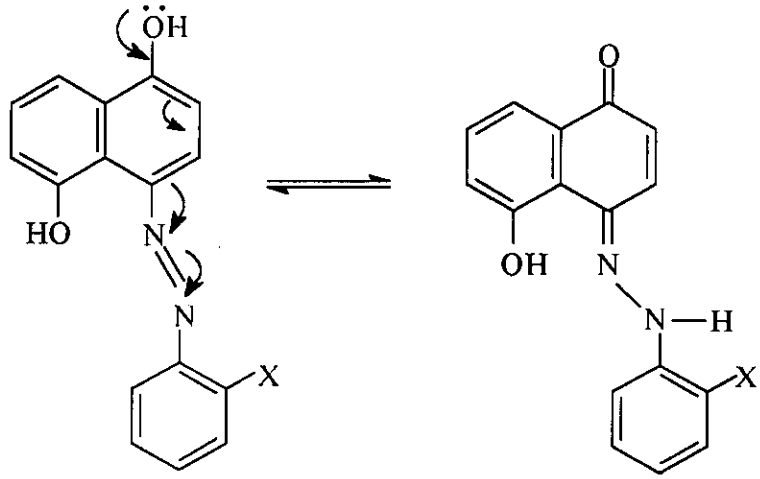
3-1- Part (A) includes the studies on the organic azo compounds and the confirmation of their molecular structure using electronic absorption spectra in organic solvents, IR and ^{1}H-NMR spectra. The electronic absorption spectra of the monoazo and bisazo compounds in ethanol exhibits four bands in the majority of cases. The first two of them are of high molar absorptivity, lie in the UV-region and are substituent independent. They are due to local excitation of the π-electrons of phenyl or naphthyl moieties of the molecules representing the ($^1L_a \leftarrow 1_A$) and

($^1L_b \leftarrow 1_A$) transtions. The third band appears as a weak one (sometimes appears as a shoulder) within the range 285-310 nm which is due to the $n \rightarrow \pi^*$ transition of the N = N and/or C = O of the substituent groups. This band is greatly affected by the nature of solvent used and disappeared in case of hydrogen bond acceptor solvents. The fourth band appears at larger wavelength and is highly affected by both solvent polarity and substitutents present in o- or p-position of azo group. This band is due to a charge transfer through whole molecule. It is found that charge migration originated from the OH group in positions 2,7-, 1,5- or 2,3- as a source to the azo group as a sink. The energy of the charge transfer is calculated theoretically and practically with a satisfactory agreement.

The effect of solvents on the electronic absorption spectra is studied in terms of different solvent parameters including microscopic and macroscopic solvent parameters. The microscopic parameters of solvent reflect the effect of polarity (π), acidity (α), basecity (β) alongwith the values of E_T or Z on the position of the charge transfer (CT) band. The plots of λ_{max} of this band as a function of such parameters show that only straight lines are obtained in case of α and β indicating that other parameters has no significant effect on the position of λ_{max} of the CT band. Also, the so-called macroscopic solvent parameters which characterise the bulk properties of the solvent such as dielectric constant (D) or refractive index (n) are investigated in the form of some functions, e.g. : F (D), ϕ (D), f (n), and $\frac{D-1}{D+1}$ these parameters are plotted against λ_{max} or $\Delta\bar{\nu}(cm^{-1})$ where it has been found that non-linear relations are obtained. This indicates that none of such parameters solely is the predominating factor affecting the position of the CT band, but the

contribution of specific solute-solvent interaction (solvation or more effectively hydrogen bonding between solute and solvent molecules) also takes place. So, the shift on the CT band position is actually the result of changed solvent polarity and the shift due to intermolecular hydrogen bond.

The CT band sometimes splits into two bands especially in compounds having strong withdrawing group in o- or p-positions with respect to N=N group. This new band is attributed to the hydrazone form of the compounds present as new species:



The substituent effect on the position of CT band has been studied in terms of Hammett constants where it is found that the position of CT band obeys the Hammett linear free energy relationship;

$$\lambda_X = \lambda_H + \rho\sigma_X^*$$

The plots of λ_{max} of the CT band against Hammett substitutent constant (σ_X^*) give a straight line with values of ρ amounting to 33.2 – 33.8, indicating that the CT band is directly affected by the nature of substituent (X). The apparently high values of ρ denotes strong

conjugation in the molecule, hence a structure that would approach a planar form.

Further confirmation of molecular structure of the newly prepared azo compounds is by use IR spectra. The important IR frequencies are assigned in relation to the expected formula of the organic compounds, the spectra are divided into four regions. In the first one (4000 – 2800 cm^{-1}) the stretching vibration of the OH and CH (aromatic) groups are assigned. The majority of OH groups show their stretching vibration at lower frequencies as a result of its participation in intermolecular hydrogen bonding with the azo group or with each other in case of azo compounds based on 2,3-dihydroxy naphthalene nucleus (Compound II_{a-h} and VI_{a-h}). On the other hand the bands found at 3165 – 2900 cm^{-1} are due to the stretching vibrations of aromatic CH groups. In the second region (1800 - 1500 cm^{-1}), the medium-strong bands within the range 1665 – 1615 cm^{-1} are assigned to the stretching vibration of the C = C ring absorption. This strong bands mask the stretching vibration band of the C=N group resulting from the hydroxy azo $\rightleftharpoons$ quinone hydrazone tautomerism which must be observed in this region. The IR spectral vibrations in the third region (1500 – 1000 cm^{-1}) comprise bands due to the C – H in-plane deformation and various skeletal vibration such as OH and the symmetric stretching modes of N = N group, which give rise to weak and variable band within the range 1460 – 1404 cm^{-1}. The OH in-plane deformation gives rise to a broad intense band at 1305 – 1255 cm^{-1}. The fourth region in the spectra (lies within the range 1000 – 625 cm^{-1}) contains most of the strong bands due to the out-of-plane deformation vibrations of the hydrogen atoms present in the ring. The band positions are assigned in terms of the number of adjacent hydrogen atoms in the ring.

The ^{1}H-NMR spectra of the monoazo and bisazo compounds were recorded in d^{6}-DMSO as a solvent using TMS as internal standard. The spectra for each group of compounds were discussed separately and the chemical shifts of the different types of protons are recorded and correlated to the molecular structure.

3-2- Part (B) of the results and discussion comprises the structure elucidation of the solid complexes formed between Co^{2+}, Ni^{2+} and Cu^{2+} with organic ligands under study.

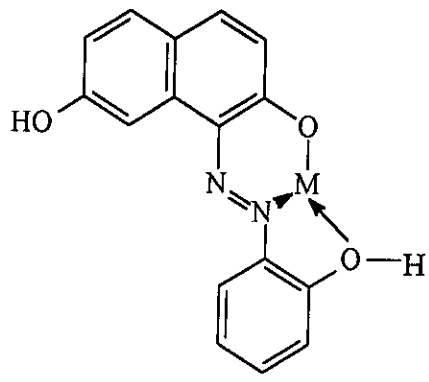
The structures of the solid complexes were firstly confirmed by elemental analysis of the isolated chelates. Data of elemental analysis show satisfactory agreement with the proposed formula. All the solid complexes are soluble in DMF but insoluble in common organic solvents and do not possess sharp melting points but decompose on heating above 350°C. The molar conductivities of the complexes in DMF indicate that some of the complexes are of ionic nature while the others are nonionic.

The stiochiometry of Co^{2+}, Ni^{2+} and Cu^{2+} complexes has been investigated by conductometric titrations which indicate the probable formation of 1 : 1 in monoazo and (2 : 1) (M : L) in bisazo compounds. The steady increase in equivalent conductance-molar ratio curves is attributed to the liberation of the easily mobile H^{+} ion through the formation of covalent bonding between oxygen atom of the hydroxyl group and metal ion in a six membered ring fashion.

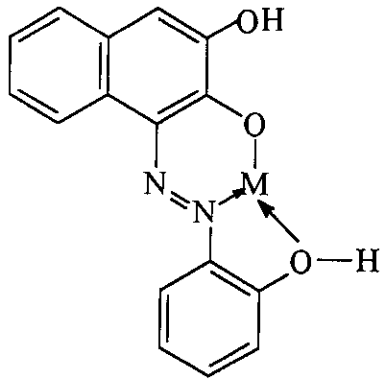
The results of thermal analysis of some selected solid chelates show that they degrade in three stages. The first step in the decomposition sequence corresponds to the loss of physically combined water molecules from the outer surface or interstice of the crystal lattice. The second step

within the temperature range 145 – 175°C represents the removal of coordinated water molecules leading to the formation of unhydrous complexes. 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 are calculated from the weight loss on the TG curves whose values are in good agreement with those obtained from elemental analysis. The $\mu_{eff.}$ values of some selected complexes show normal values for high or low spin square-planar or octahedral complexes.

The IR absorption spectra of the solid chelates have been studied and compared to those of the free ligands. For complexes with ligand molecules based on 2,7-dihydroxynaphthalene ($I_{a,b}$ and $IV_{a,b}$), the absence of the weak broad band at ~ 2900 cm^{-1} due to the hydrogen bonding OH group in case of complex species denotes the participation of this group in chelate formation. Also, the shift of the stretehing vibration ($\nu_{N=N}$) of the N=N group suggests that such ligands act as ONO donor in tridentat fashion



The azo compounds based on 2,3-dihydroxy naphthalene ($II_{a,b}$ and $V_{a,b}$) behave in similar manner to that of the previous ligands. The comparison of diagnostic IR vibrational bands indicates that chelate formation takes place as follows:



II_a

The electronic absorption spectra of Co^{2+} , Ni^{2+} and Cu^{2+} complexes are scanned in the UV- visible range. 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 Co^{2+} complexes show two broad bands within the ranges 18340 -20202 and 23809-28169 cm^{-1} corresponding to $^4T_{1g} \rightarrow {}^4A_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{2g}$ transitions in octahedral field. On the other hand spectra of Ni^{2+} complexes are characterized by two bands at 18450 -20284 and 26385 -34130 cm^{-1} due to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transitions respectively. The electronic spectra of Cu^{2+} complexes show either a band at 17452 -19157 due to the $^2A_{2g} \rightarrow {}^2B_{1g}$ transition for square planar geometry or two broad band s at 34014-20337 and 17094-20492 cm^{-1} due to $^2E_{2g} \rightarrow {}^2B_{1g}$ and $^2A_{2g} \rightarrow {}^2B_{1g}$ transitions in tetragonally distorted octahedral field.

Part C(3-3) deals with a voltammetric study of the mono and bisazo dye compounds derived from 2,3-dihydroxynaphthalene as a typical example for the other compounds. The study includes the polarographic and cyclic voltammetric behaviour of these azo dyes at mercury electrode. In polarographic measurement, the polarograms of all azo compounds

exhibited a single polarographic reduction wave within the pH range 2-11, corresponding to 4 electrons for monoazo dyes and 8 electrons for bisazo compounds except the m-CH_3 derivative. The limiting current of all azo compounds except m-CH_3 derivative is considered to be almost pH-independent. For m-CH_3 derivative, the wave height in acidic solutions is almost twice that in alkaline ones, i.e., the reduction process of this compound involves 4 or 8 electrons in acid solutions and 2 or 4 electrons in alkaline ones for mono and bisazo dye, respectively.

The effect of mercury pressure on the limiting current revealed that the limiting current is mainly diffusion-controlled with the contribution of some adsorption. Also, analysis of the polarographic wave at different pH, denoting that the reduction process is irreversible and the transfer coefficient values lie between 0.2 and 0.6. The half-wave potential ($E_{1/2}$)-pH plots revealed that, the $E_{1/2}$ shifted to more negative potential with increasing the pH denoting that the consumption of hydrogen ions in the reduction process. From the slopes of $E_{1/2}$-pH plots and these of logarithmic analysis the number of hydrogen ions participate in the rate-determining step was found to be equal to one.

In cyclic voltammetry, the voltammograms were recorded in buffer solution of pH 2.2, 6.8 and 9.2. The voltammograms of all azo compounds exhibited a single cathodic peak in all solutions. The absence of any peak in the reverse scan revealed the irreversibility of the reduction peak. Also, the irreversibility is confirmed from the shift of peak potential (E_p) on increasing the scan rate (v) to more negative values. The transfer coefficient values were calculated from the slopes of E_p-lnv plots and found in a good agreement with those obtained from dc-polarography. Also, on plotting peak current (i_p) vs. the square root of

scan rate $v^{½}$ linear correlations deviated from the origin are obtained denoting that the reduction current is not totally diffusion-controlled.

Effect of substituents on $E_{1/2}$ and E_p values was considered and it was found that the electron withdrawing group (p-COOH) shifts the $E_{1/2}$ to less negative values i.e., accelerates the reduction process, whereas electron-donating groups (p-OCH_3, p-OH, m-CH_3) shift the $E_{1/2}$ to more negative values, i.e, retards the reduction process. Also, the behaviour of m-CH_3 derivative differs from that of the other azo compounds in alkaline solutions, so 2 or 4 electrons not 4 or 8 are involved in the reduction process in such solutions for mono and bisazo compounds, respectively.

Based on the results of dc-polarogaphy, cyclic voltammetry and controlled potential electrolysis, the reduction mechanism pathway was postulated and discussed. The reduction mechanism for all compound follows the sequence H^+, e, e, H^+ with the consumption of 4 or 8 electrons for mono and bisazo compounds, respectively with the cleavage of N=N center and formation of amine. For m-CH_3 derivative in alkaline solutions the reduction occurs via the saturation of the N=N centre only to the hydrazo stage. The formation of aniline derivative was confirmed by TLC and azo dye test on the compelety electroysed solution.