CHAPTER I

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A - Literature Survey on the Polarography of Hydrazones:

The first hydrazones subjected to polarographic studies were products of the reaction between ketosteroids and **Girard T. reagent**(1,2). A number of references to the early papers on the polarography of these hydrazones are cited in the work of **Brezina et al.**(3).

According to the data obtained by **Lupton and Lynch**(4,5), unsubstituted hydrazones are reduced in acidic solutions along two waves on the polarogram, but the nature of the waves was not determined. Other investigators(6) found only one wave in the polarograms for acetone hydrazone and some other hydrazones. Benzaldehyde diethylhydrazone is characterized by a single wave its height-in alkaline solution corresponds to an addition of approximately two electrones(7) and formation of 1,1-dimethyl-2-benzylhydrazine. The currents in acidic solutions were approximately twice as large as in alkaline ones.

In the first investigations on the polarography of arylhydrazones it was found that(8-10), on storage in ethanol-water solution, they undergo changes leading to the appearance of new waves. This was first attributed to tautomeric changes. It was necessary to assume that, in the free state, phenylhydrazones of aliphatic and alicyclic ketones exist in the enhydrazine form, while the derivatives of the aromatic series and aliphatic aldehydes are hydrazones.

The tautomerism and geometric isomerism of a series of nine hydrazones were studied polarographically by **Artuzov and Kitaev**(11) in borate buffers of pH 7.20. The aliphatic members and that of cyclohexanone showed waves of half-wave potentials at -1.4 volt, which vanished with time and gave a new wave with $E_{\frac{1}{2}}$ = -0.7 volt, followed by another wave with $E_{\frac{1}{2}}$ = -1.08 volt. The aryl derivatives showed waves beyond -1.40 volt. The results obtained indicated the formation of $RR' NN=C(R'') CH R'''$ (hydrazone, $E_{\frac{1}{2}}$ -1.4 to -1.5 volt) and $RR' NNHC(R'')=CHR'''$ (enhydrazone, $E_{\frac{1}{2}}$ -1.0 to -1.3 volt).

The polarographic study of tautomerism of phenylhydrazones was continued by **Kitaev and Troepol's Kaya**(12). It was shown that the Taft treatment is applicable to reduction of the azomethine group; a plot of the sum of Taft substituent constant vs. the half-wave potentials gave a straight line for the common hydrocarbon groups. The hydrazones and enhydrazine forms were detectable on the polarograms of all substances, while the polarograms of phenylhydrazones of alicyclic ketones, aliphatic aldehydes and ketones showed the presence of waves for a third tautomeric form, the azo form. The latter gave polarographic waves of phenyl and methyl phenylhydrazones in aqueous methanol at pH 5.8-9.2 and indicated the existence of hydrazone, enhydrazone, and azo tautomers(13). Examination of the curves showed that reduction of tautomers with azo structure may occur by the addition of a proton and one electron, through a radical type intermediate. In aprotic solvents such as dimethyl formamide, the polarographic curves of the azo forms are only observed; in unbuffered solutions the azo and the hydrazone structures are detected; the enhydrazine forms are not reduced under such conditions or in alkaline buffered solutions.

Cauquis et al.(14) studied the electrochemical beaviour of a series of methylarylhydrazonomesoxalonitriles having the general formula $C(CN)_2=N-N(CH_3)-C_6H_4-X$ ($X=H$, $P-CH_3$, $m-CH_3$, $m-Cl$, $p-Cl$, $p-Br$, $p-NO_2$, $m-NO_2$ or $p-OCH_3$). With the exception of NO_2-substituted compounds, the polarograms of the titled compounds over the pH range (1.5-12.0) displayed a single well-defined four-electron, diffusion-controlled irreversible wave. The $E_{\frac{1}{2}}$-pH plots showed two linear segments intersecting at pH 4. The i_1-pH plots revealed that i_1 is practically independent of pH. In addition to the four-electron predominant wave, nitro derivatives are reduced at less negative potentials.

The polarographic behaviour of a series of ethyl-cyano-glyoxalate arylhydrazones was studied by **Bina Jain et al.**(15). The reduction of these hydrazones took place in a single four-electron well-defined, diffusion-controlled irreversible wave. The effect of different substituents on $E_{\frac{1}{2}}$ was studied through the correlation of $E_{\frac{1}{2}}$ against Hammett substituent constant and the proposed reduction mechanism is as follows:

$$X\text{-}C_6H_4\text{-}NH\text{-}N{=}C(CN)CO_2C_2H_5 + 4e^- + 4H^+ \longrightarrow$$

$$X\text{-}C_6H_4\text{-}NH_2 + H_2NCH(CN)CO_2C_2H_5$$

Sammour et al.(16) investigated the structure of 3-phenyl-2,3-diketopropionitrile-2-phenylhydrazone in aqueous ethanolic solutions of varying pH. A suggestion for the electrode reaction was given for this compound which has a true hydrazone structure in acid medium.

The electroreduction of a series of α-phenylhydrazone-β-ketonitriles in 40% by volume ethanolic aqueous buffered solutions at the DME was reported by **Fahmy and Elnagdi**(17). The results indicated that each of these compounds afforded a four-electron reduction wave in both acidic and alkaline media. In alkaline medium, this wave was attributed to the reduction of a resonance stabilized anion having considerable contribution of azo cononical form.

Malik et al.(18) studied the redox beaviour of some 2-benzothiazolhydrazones of ethyl–2-cyanoethonate in the Britton-Robinson buffer solutions of pH 2.0-4.2 and in 0.1 **M** KCl solution. It was found that the reduction occurs at the hydrazoic moiety (-NH-N=C). With respect to nitro-substituted derivatives, two waves were observed, the first corresponds to the reduction of the nitro group whereas the second wave represents the reduction of the hydrazono center. Solvent effects were also studied.

The polarographic beaviour of 4-arylhydrazono-3-methyl-1-phenyl-2-pyrazoline-5-one was studied by **Goyal et al.**(19). These compounds are reduced along a four-electron wave corresponding to the reduction of the hydrazono group in sulphuric acid as well as in alkaline buffers. The reduction process is diffusion controlled and $E_{\frac{1}{2}}$ shifted to more negative values with the increase of pH values revealing the involvement of the proton in the rate-limiting step.

The electrochemical behaviour of ethyl-2,3-dioxobutyrate-2-phenylhydrazono-3-semicarbazone was studied(20) by polarographic and voltammetric tecniques. In phosphate buffers of pH 2.2-11.8, the compound was reduced along a single wave involving fourelectrons; it was a pH-dependent process at DME. It has been reported that the reduction of hydrazono group is easier than semicarbazono center. The limiting current was independent of pH whereas the $E_{\frac{1}{2}}$ was not and shifted linearly towards more negative potential with increase in pH by 63 mV/pH.

B - Literature Survey on the Metal Chelates of Hydrazo Compounds:

The reaction of differently substituted aroyl hydrazones (R.CH=N.NH.CO.R) with nickel (II) and copper (II) salts were investigated(21). Magnetic and spectral data showed that in the case of nickel (II) chloride, octahedral complexes were formed with the ligands reacting in the keto form whereas in the case of nickel (II) and copper (II) acetate square planar complexes were obtained with the ligands coordinating trough the enol form. With copper (II) chloride, reduction took place and mono (aroyl hydrazone) copper (I) monochloride compounds were isolated.

Copper (II) celates of salicylaldehyde aroylhydrazones (H_2Sal-R) and acetylacetone aroylhydrazones (H_2Acac-R) have been prepared(22) and characterised by elemental analysis, infrared, electronic spectra and magnetic susceptibility measurements. A distorted square pyramidal structure was assigned for chelates of the type [Cu(H Sal-R)Cl.X] (X=H_2O or pyridine), whereas the anhydrous chelate [Cu(H Sal-R)Cl] was assigned as square planar arrangement. The neutral chelates [Cu(Sal-R)] and [Cu(Acac-R)], have been found to possess subnormal magnetic moments and may achieve square planar structure. In these chelates, the hydrazone molecule acts as a dibasic tridentate ligand.

The reactions of some aroylhydrazones of the type (HL) with cobalt (II) salt were investigated(23) and chelates of the types $[Co(HL)_2X_2]$ and $[Co(L)_2]$ were isolated. Analytical data, infrared studies, magnetic moments and solution spectra as well as some conductivity measurements were used to characterise these chelates. The $[Co(HL)_2X_2]$ chelates were found to possess octahedral configuration in the solid state but dissociate in DMF solutions. A dimeric pentacoordinate structure was assigned for the neutral $[Co(L)_2]$ chelates.

Complexes derived from 2-acetylpyridine hydrazone (APH) and 2-benzoylpyridine hydrazone (BPH) were prepared(24) with cobalt (II) and zinc (II) salts. The mono ligand complexes MX_2L (M=Co; X=Cl, Br; M=Zn; X=Cl; L=APH, BPH; M=Co; X=NCS; L=BPH) are tetrahedral while the bis-ligand complexes (M=Co; X=Cl, Br, NCS; L=APH, BPH; M=Zn; X=Cl; L=APH, BPH) are octahedral. These ligands appear to coordinate via both the pyridine and methylene nitrogen atoms.

The complexes of the same ligands (APH) and (BPH) with palladium (II) salts were prepared(25). Their physical properties including molar conductance measurements and spectral (ir, ^{1}H-nmr and d-d) data were discussed in terms of possible structural types and the nature of bonding. The ligands were found to coordinate in the solid state via both pyridine and methylene nitrogen atoms. A change of the bonding mode appeared to occur when the solid complexes were dissolved in DMSO.

Complexes of diacetyl bis (dimethylhydrazone) have been prepared(26) with iron (II), cobalt (II), nickel (II), copper (II) and zinc (II) salts. Their structures were examined by elemental analysis, infrared, electronic spectral measurements as well as magnetic moment determination. The complexes all have a metal to ligand ratio of 1:1 and were believed to have tetrahedral structures.

A number of diacetyldihydrazone (BDH) metal complexes of the type, $M(BDH)_2X_2$ (where M=Ni(II), Co(II); $X=Br^-$, I^-, SCN^-, NO_3^- and BF_4^-) have been isolated(27). The infrared spectra showed considerable metal to ligand interactions which were manifested by te shift of the C=N bond stretching vibration to a higher frequency region. The complexes were found to be spin free paramagnetic with nearly octahedral arrangement.

The compositions and stabilities of metal chelates of two tridentate ligands, pyridine-2-aldehyde-2-quinolylhydrazone (HQ) and pyridine-2-aldehyde-2-thiazolylhydrazone (HT) were reported(28). The mole ratio method was employed to determine the composition of the chelates formed with Cu(II), Ni(II), Co(II), Pd(II), Fe(II) and Fe(III) ions.

The high extinction coeffients of the chelates indicated their possible use for colorimetric determination of these metal ions. The acid dissociation constants were determined potentiometrically. The pk_1 and pk_2 values, determined for HT, amount 3.00 and 10.81 respectively; for HQ these values were 5.26 and 12.91. The formation constants of chelates of HQ and HT with metal ions Cu(II), Pd(II), Ni(II), Fe(II), Zn(II) and Cd(II) in 1:1 (dioxane-water) were evaluated from potentiometric titration with 0.1N sodium hydroxide.

The synthesis and characterisation of a series of Fe(II), Co(II), Ni(II) and Cu(II) complexes with N-substituted hydrazones of 2,6-diacetylpyridine were carried out(29). The analytical data included elemental analysis, infrared spectra, electronic spectra, conductivity and magnetic measurements.

Salicylaldehyde salicylhydrazone (SSH) complexes M(SSH-H), M=Cu(II), Co(II), Mn(II), VO(IV), TiO(IV); M'(SSH-2H), M'=Cu(II), Ni(II), Co(II), and Cu^{1}(SSH-H) were synthesised(30) and characterised by chemical analysis, infrared and electronic spectra and magnetic measurements. Subnormal magnetic moments have been observed in some of them. Comparison of electronic absorption bands of SSH and metal complexes showed the presence of ligand-metal charge transfer bands. Cu(II) complexes are square planar while Ni(II) and Co(II) complexes have octahedral stereochemistry. In M'(SSH-2H) complexes, infrared spectra indicated the involvement of -OH, >CO and >C=N groups. In others, only -OH and >C=N appear bonded. Metal-metal interactions via oxo-bridge structures have been discussed in the light of magnetic, electronic and infrared data.

Acetone isonicotinoyl hydrazones (AINH) were studied by **Aggarwal and Rao**(31) who found that these ligands formed complexes of the types $MCl_2.AINH.nEtOH$ and $M(AINH-H)_2.nH_2O$ (where M=Mn(II), Fe(II), Co(II), Ni(II), Cu(II) or Zn(II) and n=0, 1 or 2). $Cu^ICl.AINH$ has also been prepared starting with Cu(II) chloride. All the complexes were found to be non-electrolytes in pyridine. Tentative structural conclusions were drawn for these complexes based upon electronic structural and room temperature magnetic measurements. The ir-spectral studies denoted that AINH functions as a bi- or tridentate ligand in the complexes of the former type and as a tridentate one in the latter type of complexes. The positions of the ν(M-O) mode in the low frequency ir-spectra of the complexes have been correlated with their overall stability constants, log k.

Mihkelson(32) described the reactions of pyridine-2-aldehyde-2′-pyridylhydrazone (paphy) and its derivatives with palladium (II) in the presence of various anions. The compounds were characterised by elemental analysis, ir and mass spectrometry. In the reaction mixture, neutral species [PdLX], where paphy (HL) is deprotonated, forms first. The presence of halide and hydroxide ions facilitates the formation of the highly stable bridged species, $[Pd_3L_2X_4]$. In the bis-ligand complex $[PdL_2]$, the ligand is bidentate as shown by mass spectrometry. Preliminary solution studies indicated the existence of competing equilibria in solution.

Potentiometric and conductometric titrations of the system Pd(II) and pyridine-2-aldehyde-2'-pyridylhydrazone in aqueous solution showed(33) that only one mole of ligand coordinated with each Pd. $[PdL_2]$ did not exist in aqueous solutions. Job's method of continuous variations was applied and a computer calculation on a model system was used to estimate equilibrium constants. The pmr investigation revealed that the ligand in $[PdL_2]$ can undergo isomerisation about the imine bond.

Complexes derived from glyoxal bis (dimethylhydrazone) (GDMH) have been prepared and characterised(34), they are of the general types MX_2(GDMH) (M=Co, Zn, Cd; X=Cl, Br and M=Zn, X=SCN) and MX_2 $(GDMH)_2$ (M=Co, Ni; X=SCN). All the complexes in which the ligand is chelating as MX_2 (GDMH) are tetrahedral monomers while MX_2 $(GDMH)_2$ contain six co-ordinated metal atoms. The ligand was monoprotonated in mineral acids and the salt $[GDMH_2]$ $[CoBr_4]$ and $[GDMH_2]$ $PdBr_4$ have been isolated from acidic solution.

Hindawey et al.(35), examined the reaction products of copper (II) salts with methyl 2-picolyl ketone (2-pyridyl) hydrazone (L) and phenyl 2-picolyl ketone (2-pyridyl) hydrazone (L') by elemental analysis, magnetic susceptibility, electronic, infrared and electron spin resonance spectral measurements. The spectral data indicated a square pyramidal structure for the complexes of the type [$LCuX_2$] and [$L'CuX_2$] and a square planar configuration for the [(L-H)CuX] and [(L'-H)CuX] complexes. The complexes of stoicheiometry L_2CuX_2 and L'_2CuX_2 contained square planar L_2Cu^{2+} and L'_2Cu^{2+} units with the anions X^- in the axial positions giving distorted octahedral configurations. The complexes [$(L-H)_2Cu$] and [$(L'-H)_2$ Cu] have distorted octahedral structures in which the ligands act as monobasic tridentate.

The interaction of hydrated copper (II) chloride and bromide with phenyl-2-picolyl ketone hydrazone and phenyl-2-picolyl ketone phenyl hydrazone was studied(36) by elemental analysis, spectral studies (ir and electronic spectra) and the variable temperature magnetic susceptibility together with the electron spin resonance spectra. The complexes of the formula $[CuLX_2]_2$ were found to be dimeric through a halide bridge while those of the stoichiometry $[CuL_2]X_2$ were monomeric in nature. The magnetic data showed that dimeric complexes possess anti-ferromagnetic interaction. The mechanism of the magnetic interaction was discussed based on the variable temperature magnetic data and esr spectra.

El Dissoukey(37) reported the complexes of phenyl-2-picolyl ketone hydrazone (ppkhy) and phenyl-2-picolyl ketone phenyl hydrazone (ppkphy), with hydrated copper (II) acetate or hydrated copper (II) nitrate in mole ratio 1:1 or 1:2 (metal : ligand). Various physical techniques indicating molar conductivity, spectral (ir, electronic, esr and ^{1}Hnmr) and magnetic measurements were used to study the nature and structure of the prepared complexes.

The data showed that complexes $[CuLX_2]$, X=OAc or ONO_2 and L=ppkhy or ppkphy, were trigonal bipyramidal, $[Cu(ppkphy)_2]$ $(NO_3)_2$ was square planar and $[Cu(pphy)_2]$ $(NO_3)_2$ was tetrahedral. The acetate and nitrate groups in the mono-ligand complexes were found to be mono-and bidentate but in the ionized sphere in the bis-ligand complexes.

A number of complexes of benzil 2,4-dinitro phenyl hydrazone with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were synthesised and characterised**(38)** on the basis of elemental analysis, conductance, magnetic susceptibility, infrared and electronic spectral studies.

Tossidis et al.(39) studied the complexes formed between benzoyl-and chlorobenzoyl-di-(2-pyridyl) keto-hydrozone and Pd(II), Pt(II) and Rh(III). The complexes were characterised by chemical analysis, as well as magnetic and spectral studies and the stereochemistry of the ligand around the metal ions were evaluated. In these complexes the ligands behaved as tetradentate. The Pd(II) and Pt(II) complexes are formulated as square-pyramidal monomers, whereas Rh(III) complexes are octahedral.

Complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Pt(II) with 3- and 5-substituted salicylaldehyde benzoylhydrazones (XSBH, X=3-NO_2, 3-CH_3O, 5-Br, 5-Cl, 5-CH_3 or 5-NO_2) were reported**(40)** and characterised by elemental analysis, conductance measurements, magnetic moments (300-78k) and spectral studies. On the basis of these studies the following structures were suggested: distorted octahedral for $Mn(XSBH)_2$, dimeric, low-spin, five-coordinate for $Ni(XSBH)Cl.2H_2O$, dimeric, high-spin, five-coordinate for $Co(XSBH)Cl.2H_2O$, dimeric, four-coordinate for Zn(XSBH) and a squareplanar structure for $M(XSBH)Cl.H_2O$ [M=Cu(II) or Pt(II)].

C - Literature Survey on the Analytical Applications of Hydrazones:

In analytical chemistry, hydrazones find wide applications in detection, determination and isolation of compounds containing the carbonyl group. More recently, they have been extensively used in detection and determination of several metal ions.

The colorimetric determination of palladium (II) with pyridine-2-aldehyde-2′-pyridylhydrazone (PAP) was described(41) involving the extraction of chloro (PAP) palladium (II) from an acidic aqueous solution into o-dichlorobenzene and measurement of the absorbance of the extract solution. The compound in o-dichlorobenzene has a molar extinction coefficient of 1.65×10^4 at $\lambda_{max.}$= 562 nm. The method was suitable for the determination of 10-100 µg of palladium.

Pyridine-2-aldehyde-2-pyridylhydrazone was reported(42) as a selective reagent for the spectrophotometric determination of palladium. The composition of the complex formed in solution at pH 11.6 and 4 was determined by both the continuous variation and the mole ratio methods. Beer's law was obeyed over the range 0.8-9.6 ppm of palladium at pH 11.6. Maximum senstivity was reached in aqueous alkaline solutions of pH greater than 11. Only few metals interfere [Ni(II), Cu(II) and Co(II)] and their interference can be prevented by the addition of EDTA.

The test of pyridine-2-aldehyde-2-quinolylhydrazone (PAQH) as a selective and sensitive reagent for cobalt and nickel was reported by **Singhal and Ryan**(**43**). The reagent reacted with only few metals to give coloured complexes; with the exception of palladium. The cobalt chelate was the only relatively stable complex towards protons and PAQH was a very selective reagent for cobalt. In the presence of thioglycollic acid only nickel reacted with PAQH; the chelate was extracted with chloroform and its absorbance measured at 492 nm. The high molecular extenction cofficients ($30x10^3$ for cobalt complex and $51x10^3$ for nickel complex) permited the determination of 0.2-2 ppm of cobalt and 0.1-1 ppm of nickel.

A senstive colorimetric procedure for the determination of microgram quantities of palladium (II) with pyridine-2-quinolylhydrazone was decribed(**44**). A pH-absorbance study showed that quantitative extraction occurred at pH=1.5-2.3. Beer's law was obeyed from 0.2 to 6 ppm of Pd(II). The reaction was practically instantaneous and not senstive to variations in salt concentration.

useful as extractant. On the other hand, PDAPH formed a chelate which can be extracted into hexane or benzene and has a much greater stability to light.

Pyridine-2-aldehyde-1-thionaphthylhydrazone reacted with copper (II) in 1M hydrochloric acid to give a complex extractable into non-polar solvents such as benzene ($\lambda_{max.}$=480 nm, ϵ=6.35x10^3) and containing the metal and ligand in 1:2 ratio. It was used for absorptiometric determination of copper**(47)** in non-ferrous alloys and in salts.

Al(III) reacted with o-hydroxybenzaldehyde isonicotinoyl hydrazone (BIH), forming a yellow 1:1 complex (λ_{max} 375 nm, ϵ 12.7x10^3). A spectrophotometric method was developed**(48)** for microdetermination of 0.5-3.5 ppm of aluminium at pH 5.0. The Sandell sensitivity of the method was 0.0021 μg/cm^2. Besides many other ions did not interfere e.g. beryllium in 100 fold amount did not interfere in the determination of aluminium.

Two moles of BIH were found to react with one mole of the metal ions Co(II), Ni(II), Zn(II), Mn(II) or Cd(II), forming complexes having λ_{max} between 380 and 420 nm with molar absorptivities between 1.5x10^4 and 2.5x10^4 (except the cadmium complex which did not show an absorption maximum(49-51). Spectrophotometric and extraction studies of the complexes have been reported.

The result of the reaction between palladium (II) chloride and picolinealdehyde-2-quinolylhydrazone in basic solution was reported(52). The spectrophotometric method for measuring palladium ion with this reagent was discussed. The color formation was essentially constant over a pH range of 6.3 to 8.9. Full color development did not occur at higher or lower pH values. A study of excess of reagent on the palladium system showed that a two-fold excess of reagent was required to obtain maximum and reproducible color formation. It was found also that picolinealdehyde-2-quinolylhydrazone acted as a nonselective reagent towards transition metal ions in basic solution. Other platinum metals, ruthenium (III), rhodium (III), osmium (III) and iridium (IV) all interfered.

The synthesis, acid-base equilibria and metal-ion chelating tendencies of benzoylacetonemonohydrazone-3-hydrazino-4-benzyl-6-phenylpyridazine (BAHP) were reported(53). The values of the stability constants of some BAHP complexes with transition, non-transition and lanthanide ions have been evaluated from potentiometric measurements of hydrogen-ion concentration. Probable structures of the metal chelates were inferred from the electronic absorption spectra and infrared examination of the solid copper complex. The use of BAHP as an analytical reagent for the spectrophotometric determination of copper, nickel and cobalt ions was discussed. The color of their complexes was stable for more than 24 hrs and reached maximum intensity within 5 min of mixing. The optimum pH was found to be 3.5 for copper and cobalt and 4.0 for nickel. The systems obeyed Beer's law in the metal concentration range 0.9-10.0 µg/ml.

AIM OF THE WORK

The aim of the present investigation is to study the spectrophotometric and polarographic behaviour of some hydrazones. The possibility of using such new ligands as analytical reagents for spectrophotometric and polarographic determination of Co^{2+}, Ni^{2+}, Cu^{2+}, La^{3+}, Gd^{3+} and Pt^{4+} ions is to be examined. Different methods are used for characterizing the structural formula and geometries of the expected metal chelates formed on allowing these hydrazones to react with some metal ions, such as spectrophotometric, conductometric and thermal analysis methods. The stepwise formation constants of the chelates are to be determined potentiometrically.

The spectrophotometric and polarographic methods are to be used as methods of analysis for determination of trace amounts of these ions using the hydrazone compounds as reagents.