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# SYNTHESIS AND SPECTROSCOPIC INVESTIGATION OF SOME METAL COMPLEXES

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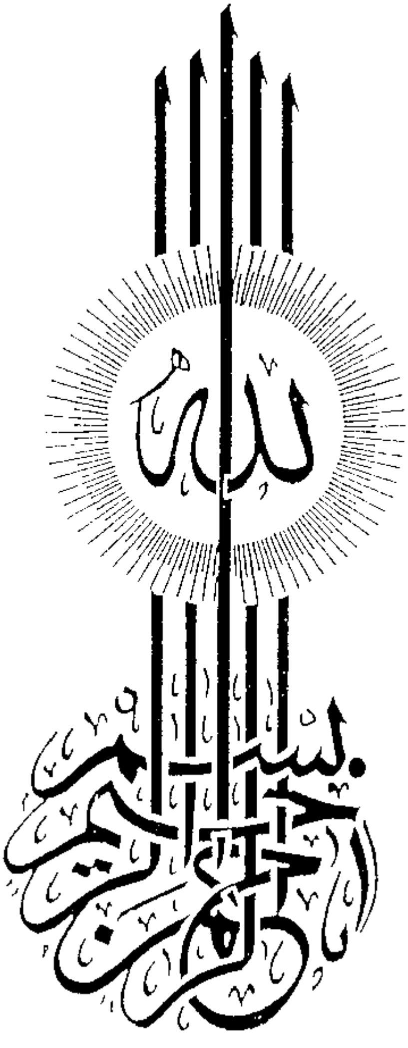

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# SYNTHESIS AND SPECTROSCOPIC INVESTIGATION OF SOME METAL COMPLEXES

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# Aim of Investigation and Problem Orientation

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It is generally accepted that the specific and selective reaction of organic reagents towards metal ions depends upon the presence and position of certain functional groups. These groups should be capable of forming co-ordination bonds. In view of this fact it seemed of interest to test the behaviour of anthranilic acid towards the reaction with some esters or ketones or their derivatives to produce the corresponding anilide or Schiff base derivatives. Each molecule of the resulting anilides or Schiff's base contains different characteristic functional groups liable to form co-ordination bonds with transition metal ions.

As a matter of fact, the transition metal complexes of aryl Schiff bases or anilides has applications as catalysis in various chemical and photochemical reactions as well as in biological systems. The applications of such metal chelates to anyone system depends to a large extent on its molecular structure. Thus, it is of large importance to get a deep idea about the structure of the formed complex.

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A clear understanding of the behaviour of the organic ligands can be obtained if the spectral characteristics of the compounds are known. For this purpose an investigation of the spectral behaviour of the ligands in the present work became necessary to proceed on with the study of their metal chelates.

In the present investigation, the effect of molecular structure on the acid dissociation constants in water-organic solvent mixture is studied. The composition, nature and stability of the complexes formed between these compounds and $Mn^{2+}$, $Co^{2+}$, $Ni^{+2}$ and $Cu^{2+}$ ions are also investigated. The suitable conditions for working out these points have been reported. Moreover, in order to gain more knowledge about the mode of bonding of the metal ions to the ligands forming the complexes some solid complexes are prepared and their structure studied by elemental analysis and physical methods such as ir absorption spectra, electronic absorption spectra, electron paramagnetic resonance (EPR), as well as thermogravimetric analysis (TGA) and X-ray diffraction.

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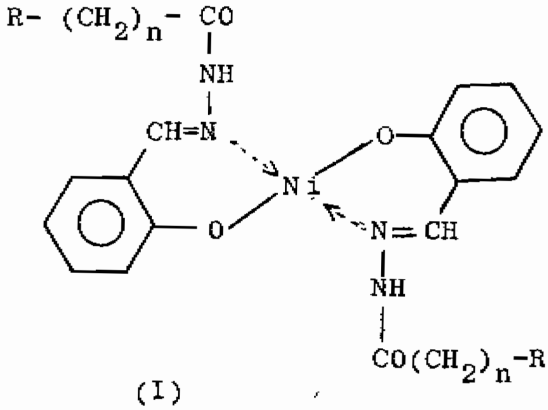
## Literature Survey on Anilides and Their Metal Chelates:

Anilides are known to form stable complexes with some heavy metal ions either in aqueous or alcoholic solutions. The study on metal complexes with organic anilides drew the attention of many investigators in a trial to solve the problem concerning their chemical structure.

The use of anilides as chelating agents drew the interest of Sacconi(1), who indicated that the reaction of anilides of the type R-CO-NH with nickel ion depended on the nature of R-groups. On treating nickel ion with anilides of the types -NH-CO- $(CH_2)_n$-R where R represents methyl or phenyl groups, the following structure (I) were formed:



(I)

The formation of bicyclic complexes when R = Phenyl and n = 0 is undoubtedly due to the greater enolizing

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# CHAPTER I

# INTRODUCTION

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In the ir spectra of the ligands, the absence of a band around 2500 $cm^{-1}$ due to $\nu_{(SH)}$ indicated the thione nature of the ligands in the solid state. The free ligands exhibited a strong band in the range 1120-1185 $cm^{-1}$ which is assigned to the $\nu_{(C=S)}$ (4). On complex formation, this band disappeared indicating co-ordination through sulphur atom with the conversion of C=S to C-S. A new band simultaneously appeared in the 655-710 $cm^{-1}$ due to $\nu_{(C-S)}$ (5,6). The ir spectra of all the ligands exhibited a sharp band around 1650 $cm^{-1}$ due to the $\nu_{(C=O)}$ and this indicated its disappearance in the complexes due to enolization and consequent co-ordination. A strong band at ~1620 $cm^{-1}$ in the spectra of the free ligands, due to $\nu_{(C=N)}$ stretch, shifted to lower energy by 5-20 $cm^{-1}$ indicating co-ordination of nitrogen atom of azomethine group of Schiff bases(7). The ir spectral data indicated that the bonding sites are O,N and S in the complexes. Thus the analytical and ir data and the valence requirement of the metal ion revealed the tridentate dibasic behaviour of the ligands.

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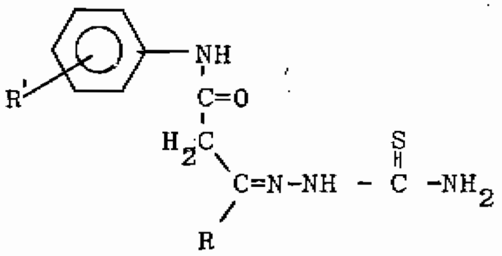

(II)

R = $CH_3$, R'=H, o-Cl, o-$CH_3O$, $OCH_3$.

R = $C_6H_5$ ,R'=H, m-$NO_2$.

Syamal et al (8) prepared cobalt (II) complexes resulting from the reaction of $CoCl_2.6H_2O$ with HL (HL= acetoacetanilide, acetoacet-o-chloro-anilide, acetoacet-o- toluidide) and the pH of the resulting solutions was adjusted to 7.4 with $NH_3$ to give $CoQL_2$ (Q = pyridine , β-picoline, γ -picoline). Also $CoQ'L_2$ where Q = o-phenanthroline and α, α'bipyridine, and HL = acetoacetanilide were prepared. Conductance measurements on the paramagnetic complexes indicate that the complexes are non electrolytes. The complexes exhibited only one ligand field band at ~ 19,500 $cm^{-1}$ corresponding to the transition $^4T_1(F) \longrightarrow {}^4T_1$ (P), the spectral data confirmed the octahedral structure of these complexes.

Mixed ligand complexes of cobalt (II), copper (II) and Zinc (II) with acetoacetanilide and some

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other nitrogen donor ligands of compositions [MX(aca CN)B ], [MX(aca CN) $(H_2O)_3$], [MX(aca CN)$B_2(H_2O)$ and[MX (aca CN) $B_3$ ], where M = Co (II), Cu (II), Zn (II), X =$Cl^-$, $Br^-$, $NO_3^-$, $ClO_4^-$, acaCN = acetoacetanilide anion, B = pyridine, $\gamma$-picoline, quinoline have been prepared by Bipin(9) The compounds have been characterised on the basis of analytical , conductance, magnetic susceptibility,ir and electronic spectral data. The thermal decompositions of a few cobalt (II) and copper (II) complexes were studied by TGA and DTA techniques.

The ir active bands at 1630 (C=0), 1590 (C=C) and 1150 $cm^{-1}$ (C-0) in acetoacetanilide appeared at $\sim$ 1620, 1580 and 1100 $cm^{-1}$, respectively in the metal complexes. Hence it was concluded that the ligand (acaCNH) was bonded to the metal ions through both the amidic and enolic oxygen atoms. The spectra revealed the appearance(10) of metal oxygen bond at $\sim$ 450 $cm^{-1}$ in the far ir region for the complexes. The sharp band observed at 3300 $cm^{-1}$(NH) in the spectrum of the free ligand and in the metal complexes indicated the non co-ordination of the amidic nitrogen atom of acetoacetanilide molecule to the metal ions. In case of some cobalt (II) and copper (II) complexes,

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the presence of co-ordinated water was ascertained by the observation(11,12) of a broad double hump at ~ 3450 $cm^{-1}$ followed by the appearance of a sharp peak at ~ 840 $cm^{-1}$. All the copper (II) complexes except the perchlorate complex showed a broad band in the 13,750 -14,300 $cm^{-1}$ region due to $^2Eg \longrightarrow {}^2T_{2g}$ transition(13) indicating a distorted octahedral stereochemistry of the complexes. A single broad band was noticed for the perchlorato complex at 15,400 $cm^{-1}$ inconformity with the spectral band for the penta-co-ordinated copper (II) complexes reported(14).

The mixed ligand complexes of the type [CuAB] X $H_2O$ (where X=0 or 2, A = amide deprotonated glycylglycine, B = glycine , alanine, serine , threonine or valine) have been isolated by Mandloi et al (15). The formula of these complexes have been proposed on the basis of elemental analysis. Co-ordination through the amino group of glycyl-glycine and secondary ligands, deprotonated amide group of glycylglycine and carboxylated group of the amino acids have been investigated on the basis of ir data. Visible spectral studies of these complexes led to the conclusion that these were of tetragonally distorted octahedral geometry in aqueous solutions.

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