GENERAL INTRODUCTION

Both acid hydrazides and Schiff bases are well known ligands in preparative chemistry because of their potentiality as coordinating agents. The antitubercular activity of acid hydrazides which are attributed to their ability to form chelates with Cu (II) ions\(^1\), has interested many authors to study the biological activity of acid hydrazide complexes. Similarly, Schiff bases have been widely employed as chelating agents to ascertain the biological significance of the \( \text{C} = \text{N} \) - grouping\(^2\). Uptil now, no ligand molecule has been utilised as a chelating agent which contains the azomethine grouping along with an acid hydrazide part in its molecule. In this work, one such ligand has been synthesised and its capability of acting as a chelating agent with transition metals, viz. Ni (II), Co (II) and Cu (II) has been studied in details.

The use of Schiff bases as chelating agents have been reported by many authors in their excellent reviews\(^3\text{-}^5\) of Schiff base complex compounds of both transition and nontransition metal ions. A brief survey of the metallic complexes of Schiff bases investigated in recent years will be given chronologically in a later section.
In the present chapter, we desire to give a brief review of the complex compounds of acid-hydrazides investigated so far.

**Acid-hydrazides as chelating agents**

The acid hydrazides have interested many workers to use them as chelating agents for transition as well as non-transition elements. As the present work is limited to some transition metals only, viz. Co (II), Ni (II) and Cu (II), we restrict the discussions on the work with the transition elements only. In an acid-hydrazide, having the general formula \( R - CO.NH.NH_2 \), there are three active sites for coordination, the ketonic oxygen, the amido nitrogen and amino nitrogen. In a number of the complex compounds of these ligands formed, the hydrazide acts as a bidentate neutral chelating agent - the ketonic oxygen and the primary amino nitrogen being the donor atoms. Many neutral complex compounds of Ni (II), Co (II) and Cu (II) are also known in which the acid-hydrazide behaves as a monobasic bidentate ligands through enolisation of the ketonic oxygen. Thus, an acid-hydrazide molecule appears to form complexes in the two forms:

\[
\begin{align*}
R - C = O \quad \text{and} \quad R - C - O \\
\text{NH} - \text{NH}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{NH} - \text{NH}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{N} - \text{NH}_2 \\
\end{align*}
\]
The particular form will be involved in the complex formation depends upon the experimental conditions employed, as well as the metal ions used. In most cases, however, the conversion of one form into the other is possible. Complex compounds in which the hydrazide acts as a monodentate ligand, donating from the ketonic oxygen or from the imidol nitrogen are also known.

The early works with acid hydrazides were to establish the antitubercular activity of them under different conditions. Different workers worked with isonicotinic acid hydrazide and established its biological activity through complex formation with Cu (II) ions. Cymerman suggested that the antitubercular activity of isonicotinic acid hydrazide may be correlated with its ability to form chelate complexes of the type

![Chemical Structure]

and that, the inability to form such complexes results in disappearance of the activity. The action of isonicotinic acid hydrazide thus appears to include an essential chelation step. If the enolisable H-atom on the amido nitrogen atom of the hydrazide be removed by an alkyl group, then chelation cannot
occur with Cu (II) ions and consequently the antituberculcular activity of the ligand disappears. Issa\textsuperscript{11} investigated the complexes of benzhydrazide and salicylhydrazide with some divalent metal ions of the first transition series by i.r. spectrophotometry. The benzhydrazide reacted with the metals with its ketonic oxygen and the nitrogen atom of the primary amino group. The phenolic oxygen in salicylhydrazide remained free in all the metal complexes. Nagano\textsuperscript{12} made an extensive study of the complex compounds of Cu (II) with isonicotinic acid hydrazide, nicotinic acid hydrazide, picolinic acid hydrazide, benzoic acid hydrazide and p-nitrobenzoic acid hydrazide. In all these compounds the acid hydrazides acted as bidentate neutral or monobasic acid ligands. As mentioned earlier, acid hydrazides may also act as monodentate ligand in many of their chelates. Dutta-Ahmed\textsuperscript{13} reported some complex compounds of acetyl and benzoyl hydrazine (hydrazides of acetic acid and benzoic acid respectively) in which the bonding with the metal occurred from $\equiv N$ - grouping of the imidol form of the ligands.

\[
R - \overset{\text{C}}{\equiv} \overset{\text{N}}{\equiv} \overset{\text{NH}_2}{\equiv} \\
\text{OH} \quad \text{M}
\]

Metal complexes of malondihydrazide have been studied by Dutta-Ahmed et. al\textsuperscript{14}. In these complexes the ligand behaves as a
bidentate ligand coordinating through the secondary nitrogen atom.

Ray Chaudhury\textsuperscript{15} described succindihydrazide complexes of some transition and nontransition elements in which the ligand coordinates from its two secondary nitrogen atoms. The reaction\textsuperscript{16} of transition metal sulfates with adipic acid dihydrazide resulted some compounds of the type $\text{M(DA)SO}_{4}\cdot\text{H}_{2}\text{O}$ and $\text{M(DA)}_{2}\text{SO}_{4}$ where $\text{M} = \text{Mn, Fe, Cu, Co and Ni}$ and $\text{DA} = \text{adipic acid dihydrazide.}$ With metal nitrates and chlorides $\text{M(DA)X}_{2}\cdot\text{nH}_{2}\text{O}$ and $\text{M(DA)X}_{2}$ ($\text{M} = \text{Co, Mn, Cu, Ni}$) were isolated by Gogorishvili et. al. Bonding from the amido nitrogen atoms of hydrazides was established by Beg et. al\textsuperscript{18} in some copper complexes of adipic acid dihydrazide.

As mentioned earlier acid-hydrazides can act as bidentate ligands both in the keto form (1) as well as in the enol form (2)

\begin{align*}
\text{R} & \equiv \text{CC'NH'NH}_{2} \quad \text{R} \equiv \text{C'N'NH}_{2} \\
\text{O} & \equiv \text{H} \quad \text{O} & \equiv \text{H} \\
(1) & \quad (2)
\end{align*}

When the primary amino group in an acid hydrazide is condensed with an aldehyde or a ketone, the enolisation of the carbonyl group in the ligand will be facilitated, since the enol form will contain a conjugated system of double bonds.

\begin{align*}
\text{R} \equiv \text{C'N'N'} \equiv \text{CR''R'''} \\
\text{OH} \quad \text{OH}
\end{align*}
Alcock\textsuperscript{19} prepared complexes of N-acyl-N'-isopropylidene hydrazine, having the keto-form type (3) and also the enol-form type (4), and observed that compounds of the type (4) were easily obtained from the compounds of the type (3).

Gogorishvili\textsuperscript{20} studied the reactions of some transition metal salts with benzoyl hydrazine both in neutral and in alkaline medium and found that, in the neutral medium the bonding occurred from the ketonic oxygen and the nitrogen of the primary amino group, whereas in the alkaline medium the ligand reacted in the enol form to give compounds of the type

\[
\begin{align*}
\text{H}_5\text{C} & \quad \text{C} \quad \text{O} \\
\text{N} & \quad \text{NH}_2
\end{align*}
\]

(M = Co, Ni)

The i.r. spectra of the compounds of the first type contained amide I bands displaced by about 20 cm\textsuperscript{-1} to the lower frequency.
region compared with the corresponding frequency of the free ligand. On the other hand, the amide I bands were not detected in the spectra of the complexes of the second type. Their spectra were found to contain an intense band at 1350 cm$^{-1}$, which was absent in the i.r. spectra of the compounds of the first type. Besides this, an intense band near 1604 cm$^{-1}$ appeared in the spectra of the second type of complexes because of the formation of C = N - grouping due to the enolisation of the hydrazide.

Kharitonov and coworkers investigated the infra red absorption spectra of cobalt (II) complexes of benzoyl hydrazine of the type

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\begin{array}{c}
\text{H}_5\text{C} - \text{C} = \text{O} \\
\text{H} \quad \text{N} \quad \text{H} \quad \text{N} \quad \text{H}_2
\end{array} & \quad \begin{array}{c}
\text{H}_5\text{C} - \text{C} = \text{O} \\
\text{H} \quad \text{N} \quad \text{N} \quad \text{H}_2
\end{array}
\end{align*}
\]

and compared their spectra in details. In alkaline medium the compound \(\text{Co} (\text{C}_6\text{H}_5\text{CO NH.NH}_2)_3 \text{Cl}_2 \cdot 2\text{H}_2\text{O}\) was converted into the complex \(\text{Co} (\text{C}_6\text{H}_5\text{CON.NH}_2)_3\), and the latter, in turn, was reconverted into the former in hydrochloric acid solution.

\[
\text{Co}^{\text{III}} (\text{C}_6\text{H}_5\text{CON.NH}_2)_3 \xrightarrow{\text{HCl}} \text{KOH} \quad \text{Co}^{\text{II}} (\text{C}_6\text{H}_5\text{CONH.NH}_2)_3 \text{Cl}_2 \cdot 2\text{H}_2\text{O}
\]

Since the reactions were carried out in air, some oxidation-
reduction also occurred.

The same authors\textsuperscript{22} also prepared a series of compounds with Ni (II), Cu (II) and Fe (II) containing different anions like Cl', Br', I' and CNS' and examined their i.r. spectra. They showed that the shift of the amide I bands in these complexes towards lower frequencies in comparison with the free ligand, was dependent upon the anions present in the compounds.

The infra red absorption spectra of the complexes of manganese (II), iron (II), cobalt (II), nickel (II) and copper (II) with m-nitrobenzoyl hydrazine had been studied in the range 400-4000 cm\textsuperscript{-1} by Kharitonov et. al\textsuperscript{23}. It was shown that the ligand behaved in the same way as benzoyl hydrazine with the above metals. Nagornaya\textsuperscript{24} refluxed metal thiocyanates with alcoholic solution of benzoyl hydrazine and isolated compounds of the composition, M(NCS)\textsubscript{2}.2L where M = Fe\textsuperscript{3+}, Co\textsuperscript{3+}, Ni\textsuperscript{3+}, Cd\textsuperscript{2+} and Zn\textsuperscript{2+} and L = C\textsubscript{6}H\textsubscript{5}CONH.NH\textsubscript{2}. The compounds were octahedral with the anions in the complex sphere. The acid hydrazide coordinated in its ketonic form. With ethyldiene and isopropylidene derivatives of isonicotinic acid hydrazide\textsuperscript{25}, complexes of the type ML\textsubscript{2}(HgX\textsubscript{4}), where M = Fe\textsuperscript{42}, Co\textsuperscript{42} and Ni\textsuperscript{42}, L = ethyldiene or isopropylidene derivative of isonicotyl hydrazide, X = SCN' and I' and NiL\textsubscript{2}(SCN)\textsubscript{2} where L = the isopropylidene derivative were prepared and characterised by chemical analysis and i.r.
The spectra were bidentate and neutral, coordinating through the ketonic oxygen and nitrogen of the $-\text{N}=$ group.

The infrared spectra of Mn$^{++}$, Fe$^{++}$, Co$^{++}$, Ni$^{++}$, and Cu$^{++}$ complexes of various tautomeric forms of oxalyl dihydrazide were examined by Kharitonov$^{36}$. In the compounds of the type $M\,(H,L)\,C\,\text{Cl}_2\cdot\text{H}_2\text{O}$, the ligand is present in the amide form, and in the compounds of the type $ML\cdot\text{H}_2\text{O}$, enolisation of the ligand occurs and it functions as a tetradentate dibasic ligand. The resultant compounds are found to contain rings of the type

$$
\begin{array}{c}
\text{H}_2\text{N} - \text{NH} \\
\text{M} \quad \text{O} \\
\text{C} - \text{C} \\
\text{NH} \cdot \text{NH}_2
\end{array}$$

in compounds having formula $M(H,L)\,\text{Cl}_2\cdot\text{H}_2\text{O}$, and rings of the type

$$
\begin{array}{c}
\text{H}_2\text{N} - \text{N} \\
\text{M} \quad \text{O} \\
\text{C} - \text{C} \\
\text{N} - \text{NH}_2
\end{array}$$

in compounds of formula $ML\cdot\text{H}_2\text{O}$.

The coordinating power of paramethoxy benzoyl hydrazine was examined by Kharitonov et al$^{27}$, using Co (II), Ni (II),
Zn (II) and Cd (II) ions. The ligand behaved analogously to benzoyl hydrazine, and in the neutral medium, it acted as a bidentate neutral ligand.

The cyanato, selenocyanato and thiocyanato metal complexes of transition metals like Mn$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ were examined by Tsintsadze et. al$^{28}$ using benzoyl hydrazine as the chelating agents. In these complexes the benzoyl hydrazine coordinates through its ketonic oxygen and the primary amino group, and the anions were coordinated to the central metal ion.

Salicylic acid hydrazide was employed by Kharitonov$^{29}$ for the preparation of complexes of transition metals like Cu (II), Co (II) and Ni (II). In the complexes the ligand was present either in the amide form or in the imino alcoholic form, depending upon the pH of the reaction medium. A preliminary study of the i.r. spectra of the complexes revealed that, in alkaline medium, complexes were formed with the deprotonated residues of salicylic acid hydrazide molecules, probably in the imino alcoholic form

$$\text{ortho} \ - \ HO - C_6H_4 - C \xrightarrow{\text{N} - \text{NH}_2} M$$

In the neutral medium, the ligand coordinated in the amide form
The Cu (II) complexes of p-methyl, p-methoxy and p-chlorobenzoyl hydrazides with the compositions Cu$_2$X$_2$.2HL [where X = NO$_3^-$, $\frac{1}{2}$SO$_4^{2-}$ and HL = H$_3$C-CONHNH$_2$, H$_3$CO-CONHNH$_2$ and Cl-CONHNH$_2$] were synthesised by Butsko$^{30}$. In all the complexes, the ligand are neutral and bidentate, coordinating through the carbonyl oxygen and the primary amino group.

Isothiocyanato complexes of certain metals like Co (II), Ni (II), Mn (II) and Cd (II) with acetyl hydrazine, o-, m- and p-hydroxybenzoyl hydrazine and o-, m-, and p-methoxybenzoyl hydrazine have been investigated by Kharitonov$^{31}$ through the i.r. spectral study. From i.r. spectra, it has been established that the hydrazides are present in the compounds in the amide form, bonded with the atoms of the complex-forming metals through the nitrogen atom of the amino group and the oxygen atom of the carbonyl group. The thiocyanato groups also enter into coordination with the central metal atoms through the nitrogen atoms.

Complexes of Co (II), Ni (II) and Cu (II) with diacetyl hydrazine have been investigated by Aggarwal$^{32}$. On the basis of their analytical, visible and i.r. spectral data, it was shown
that the ligand is dibasic and tetradentate. The Cu (II) complex has been found to be square planar, whereas the Ni (II) and Co (II) complexes are octahedral with two coordinating water molecules. The dimeric nature of the complexes have also been established.

\[ \text{M} = \text{Co}^{II} \text{ and Ni}^{II} \]

\( N,N\)-diacetyl hydrazine acts as a tetradentate dibasic ligand but an unsymmetrical diacylhydrazine, viz. \( N' \)-acetyl-\( N \)-benzoyl hydrazine may react with metal ions in the keto-enol forms I, II or III.

\[
\begin{align*}
\text{CH}_3\text{CO.NH.NH.CO C}_6\text{H}_5 & \quad \leftrightarrow \quad \text{CH}_3 - \text{C (OH)} = \text{NNH.CO C}_6\text{H}_5 \\
\text{I} & \\
\text{H}_3\text{C - C(OH)} = \text{N - N = C(OH) C}_6\text{H}_5 & \quad \uparrow \\
\text{II} & \\
\text{III}
\end{align*}
\]
With a view to investigate the behaviour of N'-acetyl-N-benzoyl hydrazine towards Ni (II), Co (II) and Cu (II), Aggarwal prepared compounds of the type $\text{M(ABH)}_2 \cdot 2\text{H}_2\text{O}$, $\text{M} = \text{Co}^{\text{II}}$ and $\text{Ni}^{\text{II}}$ and $\text{Cu(AB)}$, where $\text{ABH}_2 = \text{N}'$-acetyl,$\text{N}$-benzoyl hydrazine. The complexes were found to be polymeric in nature:

\[
\begin{align*}
\text{M} &= \text{Co}^{\text{II}} \text{ and } \text{Ni}^{\text{II}} \\
\text{In neutral medium ortho-hydroxybenzoyl hydrazine (salicyl hydrazide) acts as a neutral bidentate ligand coordinating through the ketonic}
\end{align*}
\]
oxygen and the nitrogen atom of the primary amino group. This type of behaviour of the ligand was demonstrated by Mach34 in the compounds of the type ML₂.Cl₂.nH₂O (M = Mn, Co, Ni, Cu, Zn; n = 0, 2, 3 and L = ortho-hydroxybenzoyl hydrazine).

The above ligand was also employed by Kharitonov35 to prepare compounds of two types. In neutral or weakly acidic media complexes with the composition M(HL)ₓ₂.mH₂O, where M = Cu²⁺, Cd²⁺, Co²⁺ or Ni²⁺ and X = Cl⁻, SO₄²⁻ or NCS⁻; n = 2 or 3 and m = 0, 1 or 3 were obtained. These compounds were found to contain neutral hydrazide molecules. Study of the infra red absorption spectra showed that these complexes contain molecules of salicylic acid hydrazide in the amide form, joined to the central metal atoms through the nitrogen atom of the amino group and the oxygen atom of the carbonyl group. The reactions of metal salts with salicylic acid hydrazide in weakly alkaline media gave complexes which do not contain inorganic anions, but which contain L⁻ residues. The i.r. spectra of the complexes indicated that these complexes contain deprotonated salicylic acid hydrazide residues in the imido-alcoholate form, having the rings of the type

\[
\text{ortho} - \begin{array}{c} \text{HO} \\ \text{C}_8\text{H}_4 \end{array} - \begin{array}{c} \text{C} \\ \text{O} \end{array} \xrightarrow{M} \begin{array}{c} \text{N} \\ \text{NH}_2 \end{array}
\]
The reaction of aroyl hydrazines with Ni (II), Co (II) and Cu (II) were investigated by Iskander et. al. Both bis- and tris-
Ni (II) and Co (II) chelates were isolated. Magnetic and spectral measurements revealed their octahedral structures. With Cu (II) nitrate and sulfate, aroyl hydrazines gave only bis-complexes. However, with Cu (II) chloride, both mono- and bis-chelates were obtained at low temperature while at high temperatures, oxidation-reduction reactions occurred with the formation of complexes with mixed oxidation states of copper. The aroyl hydrazines employed were benzoyl, p-nitro-, p-methoxy- and o-hydroxy-benzoyl hydra-
azines. All the ligands acted as bidentate neutral species, co-
ordinating through the carbonyl oxygen and the amino nitrogen.

Popel utilised the hydrazide of o-chlorobenzoic acid to prepare a nonionic compound of Ni (II), having the formula,
NiL₂, where L stands for the deprotonated hydrazide of o-chloro-
benzoic acid. The compound can be extracted into CHCl₃ and can be used for the photometric estimation of nickel. An extensive infra red spectral study was done by Generalova, for the complexes Cu(HL)₂Cl₂.3H₂O, Cu(HL)₂SO₄.H₂O, Co(HL)₂(NCS)₂, 
Ni(HL)₃Cl₂.H₂O. CuL₂, ZnL₂, FeL₃, HCoL₃ 1.5H₂O, HNiL₃.H₂O,
Cd(HL)₂SO₄, where HL = (ortho) HO-C₆H₄ CO NH.NH₂, and also for the complexes of the deuterated ligand, viz. Cd(DL)₂SO₄,
Co(DL)₂(NCS)₂ and Ni(DL)₃Cl₂D₂O where DL = (ortho) DO-C₆H₄CO
NH.NH₂, to make a comparative study of the i.r. spectra for the
ligand coordinating through its amide form and the enolised form. Thus, for the two possible metalloccycles, viz. I and II

\[
\text{ortho - HO - C}_6\text{H}_4 - \text{C} = \text{O}_\text{M} \quad \text{ortho - HO - C}_6\text{H}_4 - \text{C} = \text{O}_\text{M}
\]

\[
\text{NH - NH}_2 \quad \text{N - NH}_2
\]

I

II

it has been found that, in the infra red spectra of the complexes of the second type which contain deprotonated residues of an organic ligand, the "amide - I" bands are absent, since the compounds no longer contains C = O grouping. Besides, compounds of the second type contain sharp band at about 1325 cm\(^{-1}\) which are absent in the compounds of the first type. An additional band at 1610 cm\(^{-1}\) occurs in spectra of the complexes second type, which is not found in the spectra of the complexes of the first type.

Complexes of zinc (II), cadmium (II), cobalt (II) and nickel (II) with p-methoxy benzoyl hydrazine were prepared and studied by Kharitonov et. al\(^{39}\). In all the complex compounds the ligand was found to be present in the amide form.

Gogorishvili et. al\(^{40}\) prepared a series of compounds having the general formula, \(\text{MLX}_2 \cdot \text{nH}_2\text{O}\), \(\text{ML}_1 \cdot 5\text{X} \cdot \text{nH}_2\text{O}\) and \(\text{ML}_2 \cdot \text{X}_2 \cdot \text{nH}_2\text{O}\)
(M = Co, Ni, Cu; X = 0.5 SO\textsubscript{4}\textsuperscript{2-}, Cl, Br, I; L = H\textsubscript{2}N NH\textsubscript{2}(CH\textsubscript{2})\textsubscript{8}CO NH\textsubscript{2}NH\textsubscript{2}; n = 0 - 8) by treating the respective metal salts with the ligand in aqueous solution, or by the substitution reaction of CoLCl\textsubscript{2} and NiLCl\textsubscript{2} with KBr or KI. The complexes ML\textsubscript{1.5}X\textsubscript{2}nH\textsubscript{2}O were found to be dimeric. Co\textsubscript{2}SO\textsubscript{4}H\textsubscript{2}O and Co\textsubscript{2}L\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}nH\textsubscript{2}O were also studied by thermogravimetric methods.

Complex compounds of transition metal ions with succinic acid dihydrazide were prepared and studied by Tsitsishvili\textsuperscript{41}. Transition metal chlorides and sulfates reacted with succinic acid dihydrazide (L) in aqueous solution to give MLX\textsubscript{2}nH\textsubscript{2}O (M = Cu\textsuperscript{2+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Mn\textsuperscript{2+}; X = Cl\textsuperscript{-}, 0.5 SO\textsubscript{4}\textsuperscript{2-}), ML\textsubscript{2}X\textsubscript{2}nH\textsubscript{2}O (M = Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Mn\textsuperscript{2+}; X = Cl\textsuperscript{-}, 0.5 SO\textsubscript{4}\textsuperscript{2-}), M\textsubscript{2}LX\textsubscript{4}nH\textsubscript{2}O (M = Ni\textsuperscript{2+}, Co\textsuperscript{2+}, Mn; X = Cl\textsuperscript{-}, 0.5 SO\textsubscript{4}\textsuperscript{2-}). No enolisation of the ligand occurred in these complexes.

Some chelates of benzoyl hydrazine were also prepared by Karkarashvili\textsuperscript{42}, starting from some simpler compounds of Ni (II) and Co (II). Thus Co(NH\textsubscript{3})\textsubscript{5}Cl\textsubscript{2}Cl\textsubscript{2} or Co(NH\textsubscript{3})\textsubscript{4}CO\textsubscript{3} NO\textsubscript{3} were treated with benzoyl hydrazine (HL) to give CoL\textsubscript{3} which was studied by thermogravimetry. Isolation of CoL\textsubscript{2}NO\textsubscript{2}(H\textsubscript{2}O).H\textsubscript{2}O, Coen\textsubscript{2}(HL)Cl Cl\textsubscript{2}, Co(HL)\textsubscript{2}L Cl\textsubscript{2} and NiL\textsubscript{2}(HL).3H\textsubscript{2}O were also reported by the same author.

Mach\textsuperscript{43} prepared mixed complexes of o-hydroxy benzoyl hydrazide (HL) and salicylaldehyde (HQ) of Ni (II) and Co (II),
by treating ethanolic solutions of $M(HL)_2Cl_2$ with a solution of salicylaldehyde in aqueous KOH. The complexes were characterised by thermal analysis and i.r. spectra studies. The mixed complexes have the general formula $M(HL)_Q2\cdot2H_2O$, where $M = \text{Co (II)}$ and $\text{Ni (II)}$. The neutral ligand behaved as a bidentate one, coordinating through the amide N-atom and the ketonic oxygen atom.

Mixed complexes of Co (II) and Ni (II) with amino acids and carboxylic acid hydrazides were prepared by Fridman. The complexes have the composition $MAL X$, where $X = \text{Cl}^-$, $\text{NO}_3^-$ or $\frac{1}{2} \text{SO}_4^{2-}$, $L = \text{dihydrazides of malonic and oxalic acid and}$ $A = \text{deprotonated glycine, serine and methionine}$. The compounds were studied by spectrophotometric and pH-metric methods.

Shman'ko treated $\text{Ni(NO}_3)_2\cdot6H_2O$ in ethanol with $P - R C_6H_4 CO.NHNNH_2$ (R = Me, OMe and Cl) and obtained compounds of the formula $(\text{NiL}_3)(\text{NO}_3)_2$, in which $L$ functions as a bidentate ligand coordinating in the keto form.

The same authors also isolated compounds of formula $\text{Co(HL)}_3 (\text{NO}_3)_2\cdot\text{H}_2\text{O}$ and $\text{Co(HL)}_3 \text{SO}_4\cdot\text{H}_2\text{O}$ by treating the nitrate and sulfate of cobalt (II) with p-methyl, p-methoxy and p-chlorobenzoic acid hydrazides. The ligands coordinated in the keto form and acted as bidentate chelating agents.
Spectrophotometric studies of Ni solution containing acetyl and benzoyl hydrazines and malonic, succinic and adipic acid dihydrazides indicate the formation of NiL$^2+$, NiL$_2^{2+}$ and NiL$_3^{2+}$ with $L = CH_3CO \text{NH.NH}_2$, $C_6H_5CO \text{NH.NH}_2$ and adipic acid dihydrazide. The stability constants for all the complex species have also determined.

Charge transfer interaction between isonicotinic acid hydrazide and Cu$^{2+}$ was established by ESR, NMR and orbital absorption studies by Hillerbrand. It was found that, in addition to the weak interaction of Cu$^{2+}$ with the ring nitrogen atom, a charge transfer interaction of Cu$^{2+}$ with the hydrazide side chain occurs.

Schiff base - transition metal complex compounds:

Excellent reviews of complex compounds of Schiff bases of both transition and nontransition elements are available. A short account of the compounds of the Schiff bases which have not yet been reviewed until now, will be given in this section. Cu (II) and Ni (II) complexes of H$_2$fsac-R, where H$_2$fsac-R denotes the Schiff bases prepared from 3 formylsalicylic acid and alkyl amines (alkyl (R) = methyl, ethyl, hydroxy ethyl, n-propyl, n-butyl, isobutyl and sec-butyl), were prepared by Tanaka and
were studied by elemental analyses, i.r. spectra, visible spectra and cryomagnetic measurements. The complexes have binuclear structures connected by two phenolic oxygens; they have the general formula \( M_2(\text{fsac-R})_2 \). The cryomagnetic data for \( \text{Cu}_2(\text{fsac-R})_2 \) indicate the presence of strong intramolecular antiferromagnetic spin-exchange interactions.

Co (II) and Co (III) complexes of Schiff bases obtained from pyridoxal and monoamines (RNH₂) and diamines were synthesised by Yamada⁵⁵. The 1:2 type Co (II) complexes were obtained with bidentate Schiff bases with \( R = \text{isopropyl, t-butyl, cyclohexyl and p-tolyl} \). Electronic absorption spectra and magnetic moment show that they have a tetrahedral configuration. The octahedral 1:3 type Co (III) complexes were obtained with the bidentate ligands for \( R = \text{CH}_3, \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7, \text{iso-C}_3\text{H}_7 \) and p-tolyl. With quadridentate Schiff bases derived from ethylenediamine and 1-methyl ethylene diamine (propylenediamine) as the amine components, 1:1 type crystalline Co (II) complexes were obtained. They consist of low-spin square planar Co (II) complexes.

The preparation of a series of Ni (II), Co (II) and Cu (II) complexes of quinquidentate ligand obtained by the condensation of two moles of 2-acetyl pyridine with one mole of
3,3'-imino bis propylamine \( \text{H}_2\text{N} (\text{CH}_2)_3\text{NH} (\text{CH}_2)_3\text{NH}_2 \) has been reported by Prince and Stotter. The authors observed that for Ni (II), the in situ synthesis gave a complex which was different from that obtained by taking the preformed ligand molecule. The Co (II) and Cu (II) complexes formed in the two preparations were, however, identical.

The Schiff bases of the general formula \( R^1R^2\text{C} = \text{N}.\text{NH}.(=\text{S}) \). \( \text{SCH}_3 \) were employed by Iskander et al. to prepare a series of Ni (II), Co (II) and Cu (II) chelates and to investigate their structures by magnetic and spectral data. Three types of ligands with \( R^1 = R^2 = \text{CH}_3 \), \( R^1 = R^2 = \text{C}_5\text{H}_10 \) and \( R^1 = \text{CH}_3 \), \( R^2 = \text{C}_6\text{H}_5 \) were synthesised and it was found that all the ligands were monobasic and bidentate in the neutral complexes, coordinating to the central metal ion through the azomethine nitrogen and the deprotonated thiol sulfur atom. Magnetic and spectral data indicated square planar Ni (II) complexes while Co (II) afforded tetrahedral complexes and all the Cu (II) chelates possessed a dimeric pentacoordinated structure.

Bergen et al. found that the alcoholic suspension of the greenish black compound, bis (thio salicylaldehyde) Co (II) could dissolve in presence of different primary amines to produce different Schiff bases. The magnetic moment values and spectral
data of the cobalt (II) compounds, viz. Co(RN-thio salicylidiminato)$_2$, where R = p-toly, phenyl, p-MeO-phenyl and n-butyl, confirmed that in these compounds the ligands acted as bidentate ones and the compounds possessed tetrahedral geometry. For the compounds, Co-N-N'-R-bis(thio salicylaldehydato), where R = ethylene and trimethylene groups, the ligands were quadridentate and the compounds were square planar similar to Co-salen.

The magnetic circular dichroism (MCD) data of bis(R-N-salicylaldimine)-Ni (II) complexes (R = H, OH, Me, Ph, o-toly, m-toly, p-toly) and bis(salicylaldehyde) ethylenediamine Ni (II) in chloroform and pyridine solutions were employed by Kato and Sakamoto$^{59}$ for correct band assignment in electronic transitions.

Chakraborty et al.$^60$ refluxed biacetyl monoxide (CH$_3$CO.C(CH$_3$) = NOH) with copper perchlorate in presence of excess of ethylamine to obtain a needle-shaped copper compound of the formula Cu$_3$L$_3$ O ClO$_4$ where

The above Schiff base compound was found to contain a bridging structure and strong antiferromagnetic interactions among the
copper atoms were shown by the subnormal magnetic moment of the compound. The authors also condensed N-N-diethyl ethylene diamine with biacetyl monoxime in presence of Cu (II) perchlorate to obtain a dimeric compound Cu₂L²(Clo₄)₂H₂O, where

\[ L' = \text{Me—C} = \text{NO} \]

\[ \text{Me—C} = \text{N·CH₂·CH₂·N·Et₂} \]

Cu-O-Cu bridging was also found to be present in the compound and strong antiferromagnetic interactions were supported by variation of magnetic susceptibilities with temperature.

The Schiff base (H₂L) derived from 2-hydroxy-5-methyl-3-nitro-acetophenone and ethylene diamine, exhibited its tetradentate functions with Ni (II) and Cu (II) to produce square planar complexes. The chelates were thoroughly investigated by Dave et. al. The chelates were thoroughly investigated by magnetic measurements and spectral analyses. Kothari et. al. investigated the stereochemistry of the complex compounds of Cu (II), Ni (II) and Co (II) with the Schiff bases 2,5-dihydroxy acetophenone-ethylene diamine and 2-hydroxy-5 methyl acetophenone-isopropylene diamine, and suggested square planar structures of the (1:1) (metal-ligand) chelates.

Ethyl-3- (o-arsonophenyl)imino butyrate, SBH₂(I) and N-(1-methyl-3-oxobutylidene)-o-arsanilic acid SBH₃ (II)
were found to form complexes with Co (II), Ni (II) and Cu (II). Ligand (I) formed complexes of the type (SBH₂)₂M·2H₂O with Co (II) and Ni (II) and SBM·2H₂O for Cu (II). All the above compounds were found to be octahedral. The Ni (II) and Co (II) compounds were found to be polymeric and Sandhu and Sandhu suggested probable structures for the same. SBH₃ were found to form five coordinated complexes with Co (II) and octahedral complexes with Ni (II) and Cu (II). Bonding sites of the ligand in these complexes could not be definitely established.

Mohankumar et. al[64] prepared quadridentate Schiff bases by condensing ethylene diamine and isopropylene diamine with 2,5-dihydroxy acetophenone, 2,5-dihydroxy propiophenone and 2,5-dihydroxy benzophenone and used them to prepare (1:1) type complexes with Ni (II) and Cu (II). Magnetic, electronic and
and ESR spectral data indicated that the Cu (II) complexes were square planar and the Ni (II) complexes were tetrahedral.

The Schiff base ligands derived from N-substituted thiosemicarbazides were prepared by Malik and Phillips to obtain new complexes of Ni (II), Co (II) and Cu (II). The complexes were characterised by i.r. and electronic spectral data, and also by magnetic measurements. The tridentate NNS Schiff bases l-(pyrid-2-yl-methylene)-2-methyl thio semicarbazide

$C_5H_4NC = N - N(Me).C(NH_2) = S(NNMeS)$
and l-(6-methyl pyrid-2-yl-methylene)-2-methyl thio semicarbazide

$6-MeC_5H_3NC = N,N(Me).C(NH_2) = S(MeNNMeS)$
formed five coordinated complexes $NiL_2X_2$ ($L = NNMeS, MeNNMeS; X = Cl, Br$). The complexes $NiL_2X_2$ and $NiL(NCS)_2$ ($L = NNMeS, MeNNMeS; X = ClO_4, NO_3$) were found to be six coordinated. The complexes Cu (NNH(Me)$_2$S)$X_2$, where $NNH(Me)_2S = C_5H_4NC = NNH.C(HMe_2) = S$ and $X = Cl'$, Br' were prepared but their structures were not ascertained.

The bidentate Schiff base l-(benzylidene)-2-methyl thiosemicarbazide $PhCH = N,N(Me)C(NH_2) = S(PhNNMeS)$ gave the complexes $Co(PhNNMeS)_2X_2$ ($X = Cl', Br'$) for which electronic spectra
and magnetic measurements indicated tetrahedral structures.

Yamada et al. synthesized various Schiff bases from pyridoxal and different monoamines (RNH₂) and polymethyleneamines and isolated many Ni (II) complexes and described their properties. The (1:2) type complexes were obtained with R = alkyl, aryl and hydroxyalkyl groups. Electronic absorption spectra and magnetic data showed square planar configurations for the complexes, except for the complex with R = hydroxyethyl, which was found to be paramagnetic with octahedral configuration. The (1:1) type complexes were isolated with the Schiff bases obtained from polymethylene diamines. They were diamagnetic with planar structures.

Richardson found that bis(trifluoroacetyl acetone) triethylene tetramine (H₂L) can form octahedral complexes with Ni (II), having composition NiL. The nickel atom was coordinated by the four nitrogen atoms and two oxygen atoms of the deprotonated ligand.

Binuclear oxo vanadium (IV) and Cu (II) complexes, M₂(fsalap-R)(OMe) (R = H, CH₃, Cl, and NO₂) were synthesized and characterized, where H₃fsalap-R denotes 2,6-bis N-(2-hydroxy-5-substituted phenyl) imino-methyl -4 methyl phenol, by Okawa.
et al. The metal ions were found to be connected by the phenolic oxygens and a methanolate ion. Since both oxo vanadium (IV) and Cu (II) ions have one unpaired electron in each of their 3d-shells, strong magnetic exchange interactions are expected and these were confirmed by ESR spectra and magnetic measurements at different temperatures.

The action of ethylene diamine and trimethylene diamine on some Cu (II) chelates of tridentate dibasic Schiff bases like glycine-salicylaldehyde and glycine-hydroxy naphthaldehyde was examined by Dutta and Banerjee. They observed that the amine exchange reaction on tridentate Schiff base complexes gave complexes of quadridentate Schiff bases. It was found that the amine exchange reaction depends upon the substituent group present in the aromatic ring of the aldehyde moiety.

The binuclear Cu (II) complexes, Cu (fsal-NMe2)(NCS)3, Cu2(fsal-NMe2)2 (NCS)3 and Cu2(fsal-Pa) (NCS)3 were synthesised and characterised by Kida et al., where HfsalNMe2, HfsalNMe2 and Hfsal-Pa denote the Schiff bases obtained by the condensation of 2,6-diformyl-4-methyl phenol with N,N-dimethyl ethylene diamine, N,N-diethyl ethylene diamine and 2-pyridyl methyl amine respectively. Strong antiferromagnetic interactions were detected in the compounds by cryomagnetic measurements.
Patel et al. prepared bidentate Schiff bases of the type

\[ R = H, \text{o-CH}_3, \text{m-CH}_3, \text{p-CH}_3 \]

and isolated with Cu (II) ions a series of trans square planar Cu (II) chelates. The structures of the complexes were ascertained by i.r. and electronic spectral studies and magnetic measurements.

Yamanouchi and Yamada isolated new Schiff base complexes of the type \( M^{II} (X\text{-sal-2-Ppy})_2 \cdot nH_2O \), where \( M^{II} = Co^{++}, Ni^{++}, Cu^{++} \) and \( Pd^{++} \) and \( X\text{-sal-2-Ppy} = N\text{-2-(2-pyridyl)ethyl-ring substituted salicylidene iminates} \), \( X = H, 5\text{-Br}, 5\text{-NO}_2 \) for Co (II), \( X = H, 5\text{-Br}, 5\text{-Cl}, 5\text{-NO}_2 \) for Ni (II), \( X = H, 5\text{-Br} \) for Cu (II) and \( X = H \) for Pd (II). All the compounds were found to be octahedral with the ligands acting as tridentate coordinating agents.

Schiff bases obtained from 4,6-diacetyl resorcinol and \( N,N\text{-diethyl ethylene diamine, N,N-di-isopropyl ethylene diamine and diethylene triamine} \) were synthesised by Manada et al., and prepare their binuclear Cu (II) complexes where strong antiferromagnetic interactions are present.
Thaker and Bhattacharyya prepared mixed ligand complexes of the type $MLL'$ (where $L = \text{salicylaldehyde}$, $L' = 2$-$\text{OH}$-acetophenone or its methyl derivatives, $M = \text{Cu (II)}, \text{Ni (II)}$) and then treated with products with mono or diamines like $\text{NH}_3$, en and pn to get square-planar mixed Schiff base complexes of nickel and copper. The authors treated the mixed ligand complexes of $\text{Cu (II)}$ and $\text{Ni (II)}$ with salicylaldehyde and substituted acetophenones to isolate the compounds (III) and (IV).

![Diagram of the complexes](image-url)
The peculiarities for the Ni (II) square planar complexes of the above type are that all of them are paramagnetic. Neutral Schiff bases obtained by the condensation of 1,3-diaminopropane and 1,3-diamino propane-2-ol with 2-formyl pyridine (FPTN and FPTNOL) and 2-acetyl pyridine (APTN and APTNOL) were employed by Dey et al to prepare the Cu (II) complexes of the type Cu(L)ClO$_4$ and Cu(L) (ClO$_4$)$_2$, and the Ni (II) complexes of the type Ni(L)X$_2$.nH$_2$O, where L = FPTN, FPTNOL, APTN, APTNOL;
X = Cl', NO₂' or NCS'. The complexes were characterised by electronic spectra, magnetic susceptibilities, i.r. spectra, molar conductivities and elemental analyses. The ligands exhibit tetradentate functions in the complexes.

The tridentate dibasic Schiff base ligands derived from pyrrole-2-aldehyde and isopropanol amine or 2-amino-2-methyl propanol were synthesised by Shyamal and Kale to prepare some Cu (II) complexes. The authors observed that the magnetic moment values of the Cu (II) complex of pyrrole-isopropanol amine increases as the temperature is lowered, indicating ferromagnetic nature of the complex, while that of the Cu (II) complex of pyrrole-2-amino-2-methyl propanol decreases with lowering of temperature, indicating antiferromagnetic nature of the complex. The difference in magnetic properties was attributed to the presence of steric hindrance arising out of two methyl groups in the latter complex.

The preparation and properties of some Ni (II) and Cu (II) complexes of neutral Schiff base ligands, derived from the condensation of ethylene diamine with acetophenone and benzaldehyde, were reported by Dey et. al. The complexes were characterised by i.r. and electronic spectral studies, and also by magnetic measurements.
Uhlig and Machelett\textsuperscript{78} condensed two moles of salicylaldehyde with 1 mole of each of the diamines $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{NH}_2$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{NH}_2$, $\text{H}_2\text{N}(\text{CH}_2)_3\text{p}(\text{C}_6\text{H}_5)(\text{CH}_2)_2\text{NH}_2$, $\text{H}_2\text{N}\text{p-C}_6\text{H}_4\text{O-p. C}_6\text{H}_4\text{NH}_2$ and $\text{H}_2\text{N}\text{p-C}_6\text{H}_4\text{CH}_2\text{p-C}_6\text{H}_4\text{NH}_2$ and used the resultant ligands to isolate chelates of Co (II), Ni (II) and Cu (II). The properties of the chelates were compared with those of the transition metal complexes of simple salicylaldimines.

By the condensation of salicylaldehyde and acetyl acetone with (S)-(+) -cysteine ester in presence of Ni (II) ions, diamagnetic binuclear square planar Schiff base complexes were obtained by Jursik and Hajek\textsuperscript{79}. From the ligand field spectra and magnetic moment values, it was inferred that in donor solvents, the complexes exist as monomeric hexacoordinated ones. Although complexes were prepared in the presence of a base, they did not undergo racemisation.

Homonuclear and heteronuclear metal chelates of $\text{N,N'}-$bis(1-phenyl-1,3,5-hexanetricone) ethylene diimine were thoroughly investigated by Lintvedt et al\textsuperscript{80} by spectral and magnetic analyses, as well as by three dimensional X-ray diffraction studies. For homonuclear chelates, Cu (II) and Ni (II) ions were employed
and for heteronuclear chelates one of the metals taken was nickel and others were Cu (II), Zn (II) etc.

Co (II), Ni (II) and Cu (II) complexes of Schiff bases derived from 4-aryl-2-amino thiazoles and salicylaldehyde were studied by Dash and Mahapatra by spectral analyses and magnetic measurements.

The tetradentate Schiff base ligand obtained from ethylene diamine and o-amino benzaldehyde was utilised by Fischer and Elias to prepare nonionic (with Cu (II) and Ni (II)) and ionic complexes (with Co (II), Cu (II) etc.) for structural studies. The ligand exhibits tetradentate function in the complexes.

The Schiff base 2,6-pyridine diyl bis(N-hydroxy phenyl aldimine) obtained from 2,6-pyridine dicarboxaldehyde and ortho-amino phenol was synthesised by Thabet et al to study its reaction with some transition metal ions, like Ni (II), Cu (II), Mn (II) etc. and other metal ions. The ligand contains five potential donor atoms, but it was found, that only four atoms were available for bonding to metal ions.

The first example of a trinuclear copper complex having a spin doublet ground state in which the copper atoms are arranged in a strictly linear fashion was furnished by Baker and Helm
with the Cu (II) complex of the Schiff base, formed by the condensation of 2,4-pentanediione and 3-amino 1-propanol. Strong antiferromagnetic interactions were noted by the authors from subnormal magnetic moment per copper atom in the complex.

The optically active square pyramidal Co (II) complex, \( N-N'\text{-bis(salicylaldehyde)}-2-(S) 4-S\text{-methyl-4-thio-1,2-butane diiminato Co (II)} \) was synthesised and characterised by Aoi and Yoshikawa. The square pyramidal structure was established by magnetic measurements and spectral analyses.

Patel and Patel isolated some Cu (II) square planar chelates with the Schiff bases which were the condensates of 2-hydroxy 3-chloro acetophenone with aniline, \( m \)-methyl aniline and \( p \)-methyl aniline. The structures of the complexes were determined by spectral analyses.

Crystalline complexes of \( N-4\text{-methyl-2-hydroxy acetophenacylidenep-dimethyl amino aniline with Cu (II), Co (II) and Ni (II)} \) were prepared by Goel et al and the structures of the chelates were assigned by physico-chemical methods.
References


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INTRODUCTION TO THE PRESENT WORK

From the reviews of the hydrazide complexes and the Schiff base complexes given in the preceding section, it is seen that no work has been done with a ligand containing both the functions of these two catenating groups in a single molecule. One such ligand, viz. ortho-N-(salicylidene)-benzoyl hydrazine has been synthesised by us and the potentiality of the ligand as a complexing agent towards Ni (II), Co (II) and Cu (II) ions, has been studied.

From the fact that acid hydrazides resemble acid amides in their basic properties, it appears more probable that, when any compound containing both the hydrazinic - NH₂ group as well as one primary amino group, will be condensed with an aldehyde like salicylaldehyde, the primary amino group will be condensed first. With this end in view, o-amino benzoyl hydrazine (anthranyl hydrazide) was condensed with salicylaldehyde in 1:1 molar proportion and a light yellow product, viz. ortho-N-(salicylidene)-amino-benzoyl hydrazine was obtained. The fact that the condensation has not taken place with the hydrazinic-NH₂ group, is supported by the i.r. and spectral studies of the ligand. It has been observed that the product shows all the bands characteristic of
any hydrazide. Thus the bands at 1660 cm\(^{-1}\) (amide I), 1527 cm\(^{-1}\) (amide II), 1240 cm\(^{-1}\) (amide III) and the four deformation vibrations of the hydrazinic-NH\(_2\) group at 1618 cm\(^{-1}\), 1350 cm\(^{-1}\), 1110 cm\(^{-1}\) and 960 cm\(^{-1}\) present in the ligand confirms that the (condensate is ortho-N-(salicylidene)-amino-benzoyl hydrazine) hydrazine part of the product is unaffected or free. Further support is obtained by comparing the P.M.R. spectra of the ligand and benzoyl hydrazine and ortho-amino-benzoyl hydrazine. From the P.M.R. spectra of the compounds it is observed that benzoyl hydrazine in CDCl\(_3\) solution shows two signals with chemical shifts 1.2 \& (1H) and 1.6 \& (2H) with respect to T.M.S. as standard. The ligand in CDCl\(_3\) solution shows the same signals with the same chemical shifts. So it is clear that the hydrazide group is present in the ligand. In o-amino benzoyl hydrazine, besides the bands at 1.2 \& and 1.6 \&, another broad band at 4 \& which is due to the nuclear primary amino group is present and in the condensate (ligand) this broad band is absent showing the absence of the nuclear primary amino group in the ligand. So, the ligand is taken to be the Schiff base of the hydrazide as shown by the following structure:

![Schiff base structure](image)
As with other hydrazides, the enolisation of this ligand is expected to occur as follows:

![Chemical structures](image)

But, as there is another -OH group in the ligand (the -OH group of the salicylaldehyde fraction), the i.r. spectra could not provide any unambiguous support in favour of the enolisation. However, it has been observed that as the pH of the alcoholic solution of the ligand is increased, the light yellow colour of the solution deepens. This is an indication for enolisation, due to the fact that, as enolisation takes place, the imido nitrogen of the hydrazide part of the ligand becomes conjugated with the benzene rings and this sequence is not present in the keto form of the ligand. Consequently, the keto form (I) will be light coloured in comparison with the enol form (II) of the ligand. So, the isolated ligand may be expected to exist as an equilibrium mixture of the keto form and the enol form. The ligand, in the enol form, can, therefore, act as a dibasic ligand.
in alkaline medium and during complex formation under such condition, deprotonation of the two -OH groups, occurs. The most striking feature of the ligand, is that it can exhibit tetra-, tri-, bis-, and mono-dentate functions depending upon the pH of the medium and the metal-ligand concentration ratio. In non-acidic medium the ligand can form non-ionic complexes in which the metal-ligand ratio are found to be (1:1), (1:2) and (1:3) depending upon the initial metal-ligand concentration ratio and pH of the medium during the reaction.

Striking difference in the complexing behaviour of the ligand in acidic and nonacidic medium has been noticed. In acidic medium enolisation of the keto group in the hydrazide part of the ligand does not appear to take place, and as such complexes of the metal:ligand ratio 1:1 are found, where the bonding from the Schiff base part as well as the hydrazide part takes place. The general formula for the compounds are found to be M(LH)X .nH_2O where M = Co (II), Ni (II) and Cu (II), n = 0, 1, 2 and 2.5 and LH = ![Diagram](image)

X = Cl', Br', I' and ClO_4'.

Detailed studies revealed that the compounds are binuclear, with the formula M(LH)_2.MX_2.nH_2O and the metal atoms are connected by
oxygen bridge. This type of Schiff base complexes where oxygen-bridging is present, has been reported by many authors\(^2\)\(^-\)\(^7\). Of the two metal atoms present, one is octahedral, and the other is pseudotetrahedral. As this type of oxygen bridged complexes are formed by many Schiff bases, this property of the present ligand reflects its characteristics of the Schiff bases.

In neutral medium, the ligand behaves as a typical hydrazide. As appreciable enolisation of the ligand occurs even in the neutral medium, non-ionic complexes of the type \(M(L^*H)_2 \cdot nH_2O\), where \(M = \text{Co (II)}, \text{Cu (II)}\) and \(\text{Ni (II)}\) and \(n = 0, 1\) and 2 are formed. This type of non-ionic hydrazide complexes have also been reported by many authors\(^8\)\(^-\)\(^10\).

In these cases, the ligand acts as a bidentate monobasic coordinating agent towards the metal ions Ni (II), Co (II) and Cu (II). The bonding occurs from the deprotonated enolic hydroxyl group and the hydrazinic \(-NH_2\) group. The Schiff base part of the ligand remains unaffected during bonding. Taking the initial metal-ligand concentration ratio 1:1, and making the pH of the
medium about 8-9, compounds of the type M(L),nH₂O can be isolated. Here the ligand exhibits tetradentate function, using the two deprotonated hydroxyl groups, azomethine nitrogen and the hydrazinic -NH₂ group as the bonding sites.

The most peculiar behaviour of the ligand is that, if the ligand concentration be taken three times the metal concentration and the pH of the solution be adjusted at about 8.0 with the addition of sodium acetate in the alcoholic solution, compounds are formed in which the metal-ligand ratio is (1:3). In these cases, the ligand molecules behave differently towards the metal ions. One of the ligand molecules acts as a tridentate moiety in the complexes and the other two as monodentates. The tridentate molecule attaches the metal ion through the two deprotonated hydroxyl groups and the azomethine nitrogen. The other two neutral ligand molecules coordinate through the ketonic oxygen of its hydrazide part. The 1:1 and 1:3 type complexes are dimeric in nature.

From the complex-forming capability of the ligand, it is clear that the ligand exhibits the coordinating property of both hydrazides as well as Schiff bases.

Before proceeding to give an account of the metallic complexes of the ligand, the preparation and a few important
properties of the ligand are briefly discussed.

**Preparation of the ligand:**

**Preparation of ortho-amino benzoyl hydrazine** - Methyl anthranilate (0.2 mols) and hydrazine hydrate (0.3 mols) were refluxed for about two hours when a clear uniform solution was obtained. This was cooled to room temperature, shaken vigorously and kept in an ice bath for about an hour. A white crystalline precipitate was obtained. This was filtered in a suction and recrystallised from ethanol when shining white crystals were obtained.

**Preparation of ortho-N-(salicylidene)-amino benzoyl hydrazine** - To an alcoholic solution of 30 gms of ortho-amino benzoyl hydrazine, 24 gms of freshly distilled salicylaldehyde was added dropwise with vigorous shaking and occasional cooling. The mixture was cooled to room temperature and finally kept in an ice bath for 2-3 hours. A yellowish product separated out, which was filtered and recrystallised from ethanol. Light yellow crystalline solid, melting at 162°C, was obtained.

**Properties of the ligand:**

(1) The ligand is a light yellow coloured crystalline solid, m.p. 162°C.
(2) It is an equilibrium mixture of two forms viz. the keto form and the enol form:

\[
\begin{align*}
\text{(Keto form)} & \quad \text{CO. NH- NH}_2 \\
\text{(Enol form)} & \quad \text{C (OH) = N. NH}_2
\end{align*}
\]

(3) The ligand is highly soluble in acetone, methyl and ethyl alcohols, but is sparingly soluble in chloroform. The ligand also dissolves in dilute HCl and dilute alkali solutions. In acid solution the colour of the ligand is light yellow, whereas in alkaline solution deep yellow colour develops, indicating enolisation. The alcoholic and acetone solutions of the ligand are acidic to litmus. Unlike other Schiff bases, the ligand is stable in acidic and alkaline solutions.
References


