

## *Chapter – II*

### **LITERATURE SURVEY**

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## LITERATURE SURVEY

Metal complexes of a wide variety of organic ligands have significantly contributed to the development of modern coordination chemistry. Among the forerunners of organic ligands, are the heterocyclic compounds and their derivatives, with a particular reference to Schiff bases. These derivatives and their metal complexes have received much attention by researchers mainly because of their synthetic feasibility, structural diversity, bonding variability, catalytic capability and varied bioactivity<sup>1-15</sup>.

The present investigation deals with synthesis and characterization of metal complexes formed of Schiff base derivatives of sulfonamides, hydrazides and pyrazinamides. Therefore, a brief survey of literature on the ligating behavior of these systems is presented in the following paragraphs.

Metal complexes derived from Schiff bases have been known for about a century and a half. Ettling<sup>16</sup> in the year 1840 isolated a dark green crystalline product from the reaction of cupric acetate, salicylaldehyde and aqueous ammonia which was undoubtedly bis(salicylaldimino) Cu(II). The corresponding complexes with phenyl and aryl derivatives of ammonia were isolated in 1869 by Schiff<sup>17</sup> who established 1:2 metal-ligand stoichiometry. In this work, Schiff discovered an exceedingly important synthetic technique of preparing salicylaldimine complexes by reaction of the preformed metal salicylaldehyde compound with primary amine. Subsequently, Schiff<sup>18</sup> prepared complexes with the condensates of urea and salicylaldehyde. Delepine<sup>19</sup> in 1899 prepared the Cu(II)-salicylaldimine complexes of 1:2 metal-ligand stoichiometry with methyl and benzyl derivatives of ammonia.

After a period of relative inactivity, the systematic synthetic study of Schiff base complexes was initiated by Pfeiffer and co-workers in 1931. Just prior to this date, Zetsche et al.<sup>20</sup> in 1925 reported the colored products from the reactions of transition metal ions and a variety of substituted salicylaldehyde Schiff bases. In 1931 Dubsy and Sokol<sup>21</sup> isolated N,N –bis(salicylidene)ethylenediamino Cu(II) complex and showed the ligand acting as a binegative and tetradentate one. Pfeiffer and his co-workers<sup>22,23</sup>, during the period 1931-1942, produced a prodigious number and a variety of complexes with Schiff bases of salicylaldehyde and its substitution products, o-aminobenzaldehyde and pyrrole-2-aldehyde.

Of all Schiff base complexes, those derived from salicylaldimines have been, by far, the most thoroughly studied and a variety of physico-chemical investigations of these complexes have served to provide a fairly clear understanding of their stereochemical and electronic properties. Indeed, the particular advantage of the basic salicylalimine ligand system has been considerable flexibility of the synthetic procedure which has allowed the preparation of a wide variety of complexes with a given metal whose properties are dependent on the detailed ligand structure.

A large number of Co(II) complexes with tetradentate ligands have been prepared, the main incentive for their preparation being the unusual oxygen-carrying property displayed by some. The oxygen-carrying properties of these substances have been reviewed<sup>24,25</sup>.

Pd(II) and Pt(II) complexes of bis-bidentate salicylaldimine complexes such as  $M(R\text{-sal})_2$  where  $M = \text{Pd}$  or  $\text{Pt}$  and  $R = \text{ethyl, n-pentyl, isopropyl or t-butyl}$  have been reported which are all diamagnetic<sup>26</sup>.

The Zn(II)-salicylaldimine complexes have been little studied owing to the closed shell configuration of Zn(II). The bis bidentate complexes of the metal are usually tetrahedral<sup>27</sup>. However, the structure of  $\text{Zn}(\text{sal})_2 \cdot \text{en} \cdot \text{H}_2\text{O}$  has been shown to be square pyramidal<sup>28</sup> due to the steric constraints imposed by the organic ligand. Lindoy<sup>29</sup> has reviewed the role of metal ions in the synthesis of various Schiff base complexes.

Pujar and Bharamgoudar<sup>30</sup> have reported the synthesis and characterization of Fe(III), Co(II), Ni(II) and Cu(II) complexes with a Schiff base derived from 5-phenylazosalicylaldehyde and aniline. The complexes have been suggested to possess either dimeric or linear structures.

Schiff bases obtained by condensing chloroanilines and toluidines with salicylaldehyde have been interacted with dioxouranium(VI) and the resulting species characterized by elemental analysis, spectral and conductance data<sup>31</sup>. The ligands bond to the metal through hydroxyl oxygen and imine nitrogen. The complexes with coordination number eight have been assigned a hexagonal bipyramid structure.

Rai et al.<sup>32</sup> have carried out the synthesis and characterization of the divalent Co, Ni and Cu complexes of Schiff bases derived from 3-hydroxyiminobutane-2-one and aniline and toluidines. The complexes are associated with octahedral geometry with some amount of tetragonal distortion.

Complexes of divalent Co, Ni, Cu, Fe, Mn, Cd and Hg ions with Schiff bases derived from benzoin and 2-amino-5-phenyl-1,3,4-oxadiazole and 2-amino-5-(*p*-anisil)-1,3,4-oxadiazole have been prepared and characterized<sup>33</sup>. The ligands are tridentate with ONN sequence. Co, Ni, Cu, Fe and Mn complexes are octahedral while Cd and Hg complexes are tetrahedral.

Patel and Patel<sup>34</sup> have interacted divalent Cu, Ni, Co, Zn and Mn ions with a polymeric Schiff base derived from 5,5-methylenebis(3-bromosalicylaldehyde) and hexane-1,6-diamine. The ligand shows tetradentate behaviour coordinating with the metal ions through its azomethine and deprotonated phenolic groups. The geometry and the thermal stability of the complexes have been arrived at.

The complexation behaviour of acetophenone glycine and acetophenone alanine towards divalent Fe, Co, Ni, Cu, Zn and Hg has been studied<sup>35</sup>. The ligands show dibasic, tridentate behaviour with ONO donor set. Fe, Co, Ni and Cu complexes are dimeric while Zn and Hg complexes are monomeric.

Chohan and Mushtaq<sup>36</sup> have reported a series of biologically active pyrazine-based Schiff base ligands by the condensation reaction of 2-aminopyrazine and salicylaldehyde and acetamidobenzylaldehyde and their Co(II), Ni(II) and Zn(II) complexes. The biological evaluation of the ligands and the complexes has been made against the bacterial strains: *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*.

Cu(II), Ni(II), Co(II) and Mn(II) complexes of Schiff bases derived from dehydroacetic acid and aniline, p-chloroaniline, p-iodoaniline and p-phenetidine and characterized by various physicochemical data<sup>37</sup>. All the complexes have been reported to have an octahedral geometry, the Mn(II) complexes being with dimeric nature.

Raman and Thangarajan<sup>38</sup> have reported a novel 14-membered macrocyclic Schiff base derived from 3-cinnamalideneacetanalide and o-phenylenediamine - a tetradentate and strongly conjugated ligand to form a cationic solid complexes with Cu(II), Ni(II), Co(II) and Zn(II). The complexes have been structurally and biologically evaluated showing higher activity than the ligand.

VO(IV), Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II) and Hg(II) complexes of Schiff base derived from 4-aminoantipyrine and 3-hydroxy-4-nitrobenzaldehyde have been reported and their structural features obtained from elemental analysis, magnetic susceptibility, molar conductance and mass, IR, UV-Vis, <sup>1</sup>H NMR and ESR spectral data<sup>39</sup>. The data show that the complexes have a composition of ML type. Square planar geometry has been suggested for all the complexes with the exception of VO(IV) complex which has square pyramidal geometry.

Metal complexes ML<sub>2</sub>Cl<sub>2</sub> where M is Fe (II), Co (II), Ni(II), Cu(II), Zn(II) and Cd(II) and L is the Schiff base formed by the condensation of 2-thiophenecarboxaldehyde with 2-aminopyridine or N-(2-thienylmethylidene)-2-aminopyridine have been studied<sup>40</sup>.

Transition metal complexes of Schiff bases derived from 2-formylindole, salicylaldehyde and N-aminorhodanine have been prepared and characterized by elemental analysis and various spectral data<sup>41</sup>. The systems prepared have also been screened for antimicrobial activity against *Bacillus cereus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Candida albicans*. The results

have indicated that the ligands have no activity whereas their complexes are with significant activity.

Tahira et al.<sup>42</sup> have reported Co(II), Ni(II), Cu(II) and Zn(II) complexes of a Schiff base derived from sulphadimidine and benzaldehyde. The structural features of the complexes have been established from elemental analysis, magnetic susceptibility, conductance, IR and electronic spectral data based on which an octahedral geometry has been proposed.

The synthesis and characterization of divalent Co, Cu, Zn and Hg complexes of a Schiff base ligand derived from pyrazinamide and salicylaldehyde has been reported<sup>43</sup>. An octahedral geometry to the Co(II) complex, a Square planar geometry to Cu(II) complex and a tetrahedral geometry to the Zn(II) and Hg(II) complexes have been proposed.