

SYNTHESIS AND CHARACTERIZATION OF SALICYLALDEHYDE AND 2,4-DINITROPHENYL HYDRAZINE SCHIFF BASE WITH ITS COBALT (II) AND MANGANESE (II) COMPLEXES

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ABSTRACT

The synthesis of Schiff base derived from salicylaldehyde and 2,4-dinitrophenyl hydrazine and its metal complexes were undertaken. This synthesis was achieved via the reflux condensation of salicylaldehyde and 2,4-dinitrophenyl hydrazine. Two metal complexes were prepared by coordinating the as-synthesized ligand with Cobalt (II) and Manganese (II) ions. The structures of the prepared ligand and the complexes were confirmed from the Fourier transformed infrared analysis. A laboratory tests were employed to study the melting and decomposition temperatures, Solubility, conductivity and magnetic susceptibility. The ligand obtained was a pale orange in colour with a percentage yield of 67% and melting point of 220°C, The Cobalt(II) complex was found to be Orange in colour with 89% percentage yield and 250°C decomposition temperature and the Manganese(II) complex was found to be a deep orange colour with 81% percentage yield and 246°C decomposition temperature, The ligand and the complexes were found to be insoluble in water and slightly soluble in some common organic solvents, All the complexes are found to be paramagnetic in nature.

Keywords: Ligand, Complexes, Cobalt, Manganese, Salicylaldehyde, 2,4-dinitrophenyl hydrazine

INTRODUCTION

Schiff bases play a vital role in the field of coordination chemistry. This is due to their numerous industrial and biological applications, they have received extensive researches. Hugo Schiff was the first to describe Schiff bases, which are the condensation products of primary amines with carbonyl compounds (Cimerman et al., 2000). The azomethine group, which has the generic formula $RHC=N-RI$ and may be substituted in a number of ways, is what unites these compounds structurally. Where R and RI may be alkyl, aryl, cyclo alkyl, or heterocyclic groups. These substances are also known as azomethines, imines, and anils. Studies by Singh et al. (1975), Perry et al. (1988), Elmali et al. (2000), Patel et al. (1999), Valcarcel et al. (1994), Spichiger et al. (1998), and Lawrence et al. (1976) demonstrated that, the presence of a lone pair of electrons in an sp^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Schiff base is a nitrogen analog of an Aldehyde or ketone in which the $C=O$ group is replaced by $C=N-R$ group. It is formed by the condensation of carbonyl compounds with a primary amine. The formation of a Schiff base from is a reversible reaction and generally takes place under acid or base catalysis, or on the application of heat. Schiff bases typically contain ligands that can form very stable complexes with transition metals, such as bidentate, tridentate, Tetradentate, or polydentate.

They can only operate as coordinating ligands if a functional group, often the hydroxyl, is located close enough to the point of condensation to allow for the formation of a five- or six-member ring during reaction with a metal ion.

According to Cimerman et al. (2000) and Elmali et al. (2000), a wide range of areas, including biological, inorganic, and analytical chemistry, use Schiff bases produced from aromatic amines and aromatic Aldehyde. Many novel analytical devices have applications that call for the presence of organic reagents as crucial components of the measuring system. In coordination chemistry, Schiff bases are frequently used as ligands (Andruhe et al., 2005). This is due to their accessibility, adaptability, and tunable qualities, which depend on the precursors (primary amine and carbonyl compounds). They display a variety of reactions and capabilities. Additionally, the quantity, type, and relative positioning of a Schiff base ligand's donor atoms allow for effective control over the stereochemistry of metallic centers as well as the total number of metal ions present in homo- and hetero poly nuclear complexes. According to Akmalet al. (2007), these properties make Schiff bases excellent ligands for the formation of metal complexes that are useful in bioinorganic chemistry, catalysis, encapsulation, transport, and separation processes. Hydrazones are used as multi dentate ligands for transition metals in colourimetric or fluorimetric analyses in analytical chemistry.



Figure 1: General structure of the Schiff base

MATERIALS AND METHODS

All chemicals in this research work were of analytical reagent grade and are used without further purifications.

Preparation of reagent

(3g) = (2.98g) of 2,4 dinitrophenyl hydrazine was accurately measured in a washed 250ml conical flask and dissolved in

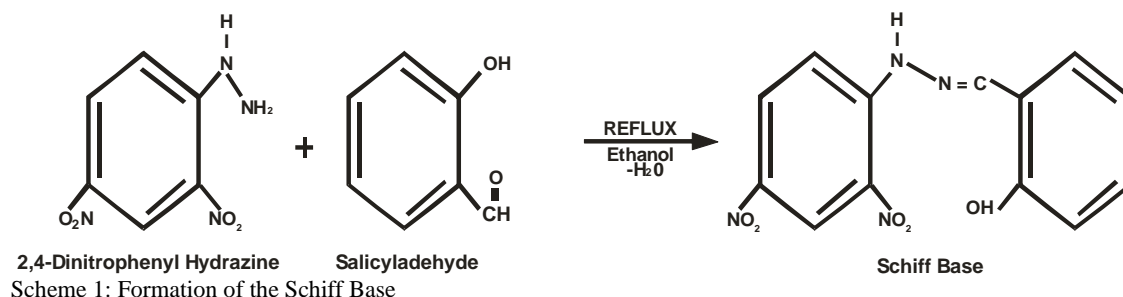
with (50ml) of ethanol, (5ml) of concentrated HCl was added and cleared solution was formed upon continue stirring for about 15 minutes.

Synthesis of the Schiff Base

By condensing an equimolar mixture of salicylaldehyde (0.1 ml) and 2,4-dinitrophenylhydrazine (0.10 mmol=1.198 g),

followed by the addition of 30 ml of ethanol and one hour of refluxing, the Schiff base ligand was generated. The resulting orange crystalline substance was filtered, washed with

ethanol, Recrystallized from ethanol, and dried for three days in a phosphorus-containing desiccator. The reaction equation is shown in scheme 1.

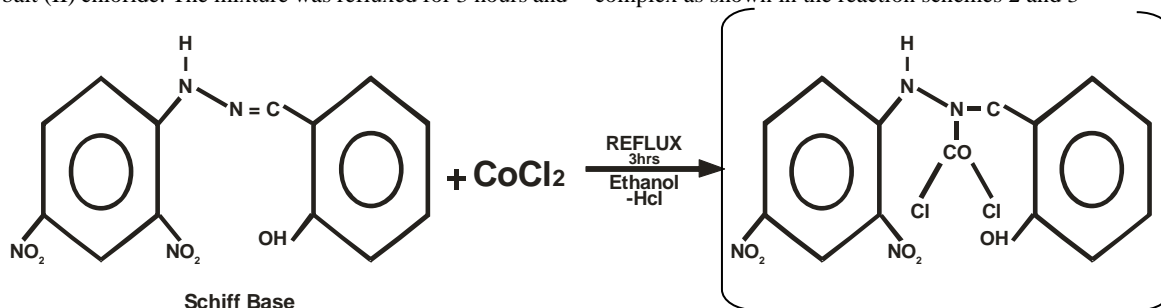


Scheme 1: Formation of the Schiff Base

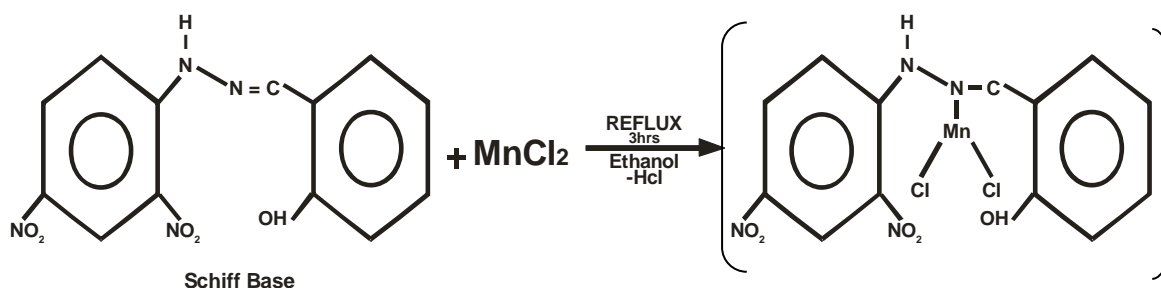
Synthesis of the cobalt (II) complex

The Cobalt (II) complex was prepared on 1:1 molar ratio of metal to ligand. 2.0g (0.0056mol) of Schiff base ligand was added in 50 ml of ethanol and mixed 1.34 g (0.0056mol) of a cobalt (II) chloride. The mixture was refluxed for 3 hours and

then cooled at room temperature. The product obtained was filtered, washed with ethanol. Crystallization from aqueous ethanol gives the desired metal complex. The same procedure was employed for the synthesis of the Manganese (II) complex as shown in the reaction schemes 2 and 3



Scheme 2: Formation of cobalt (II) complex



Scheme 3: Formation of Manganese (II) complex

Laboratory tests for variables

Different solvents such as Ethanol, Methanol, Acetone, Ester and dimethylsulfoxide (DMSO) were used to test the solubility of the complexes such that; 0.2 g of the samples were added in a test tubes containing 5 ml of the solvents and vigorously stirred for 30 minutes to establish the solvation/hydration equilibrium. The melting points and decomposition temperatures of each sample was determined using a glass capillary tube placed in SMP10 melting point machine. The molar conductivity measurement of the metal (II) complexes was carried out using 0.1g of each of the prepared compounds, then dissolve in dimethylsulphoxide (DMSO) in a test tube, and the electrode was inserted, and the reading was recorded. The various temperature of melting and decomposition of each sample were presented in table 1. Magnetic susceptibility data of the Compound was collected at room temperature using MBS MK1 magnetic susceptibility balance. Experimental method used to determine susceptibility balance is as follows:

The contribution of the magnetic field produced by a substance is called its magnetic susceptibility. Magnetic susceptibility is measured using Gouy balance.

There is a relationship between the measured magnetic susceptibility and gram magnetic susceptibility (X_g) given by;

$$X_g = \frac{C_{\text{Bal}}(L)(R-R_0)}{10^9 M}$$

Where; C_{Bal} = Balance calibration constant = 1.0

L = Height of the sample in tube (cm)

R = Reading for tube and sample

R_0 = Reading for empty tube

M = Mass of the sample (g)

From the knowledge of gram magnetic susceptibility (X_g), molar magnetic susceptibility (X_m) can be calculated using the relation. $X_m = (X_g) \times (\text{Molar mass})$

Where; X_g = Gram magnetic susceptibility

X_m = Molar magnetic susceptibility

Note that when (X_g) is negative, then it indicates that its diamagnetism likewise if (X_g) is positive, then it indicates that its Paramagnetism while R_0 is always negative because glass is diamagnetic in nature.

Infrared Spectroscopy

The infrared absorption spectroscopy of the prepared ligand and the complexes were carried out at the Scientific research laboratory, Bayaro University, Kano, using a Cary FT-IR-630 model spectrometer, at the region of 4000–650 cm^{-1} Diamond Crystals disc. Infrared spectroscopy is an extremely powerful

analytical technique for both qualitative and quantitative analysis. The infrared spectrum of the prepared samples were interpreted by the use of known functional group frequencies. The infrared absorption frequencies are shown in the table 3.

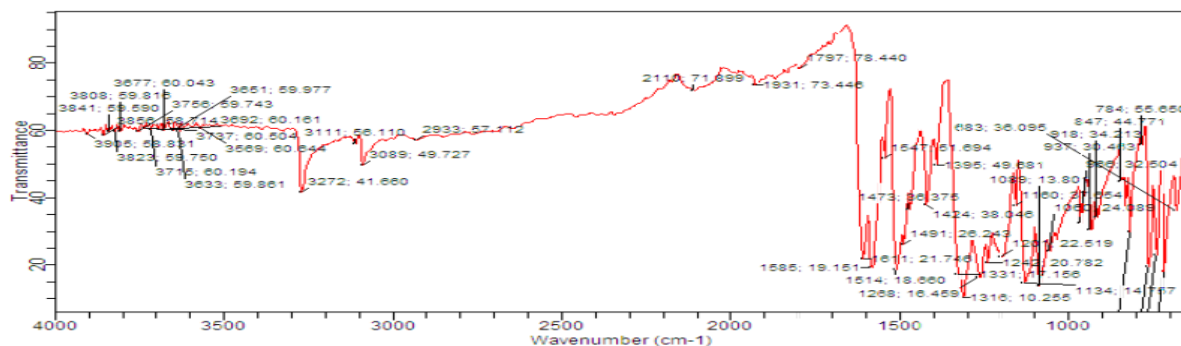


Figure 2: FT-IR spectra of the Schiff base

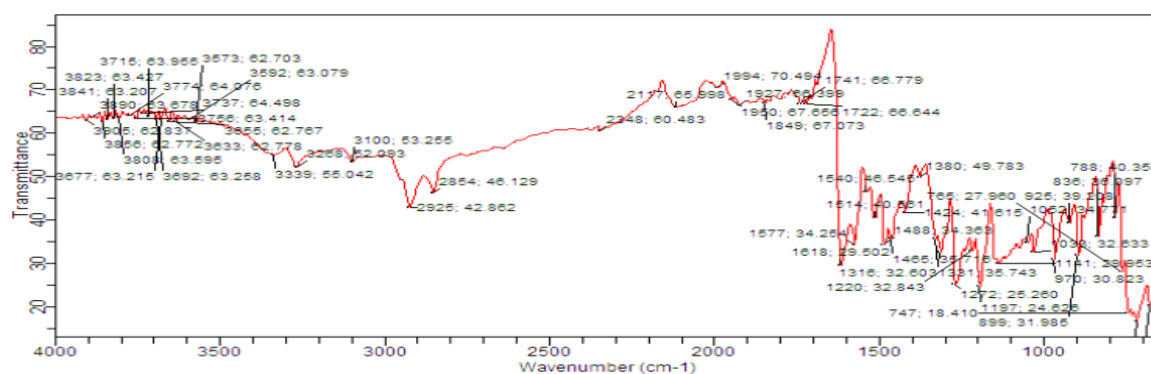


Figure 3: FT-IR spectra of the Co (II) Complex

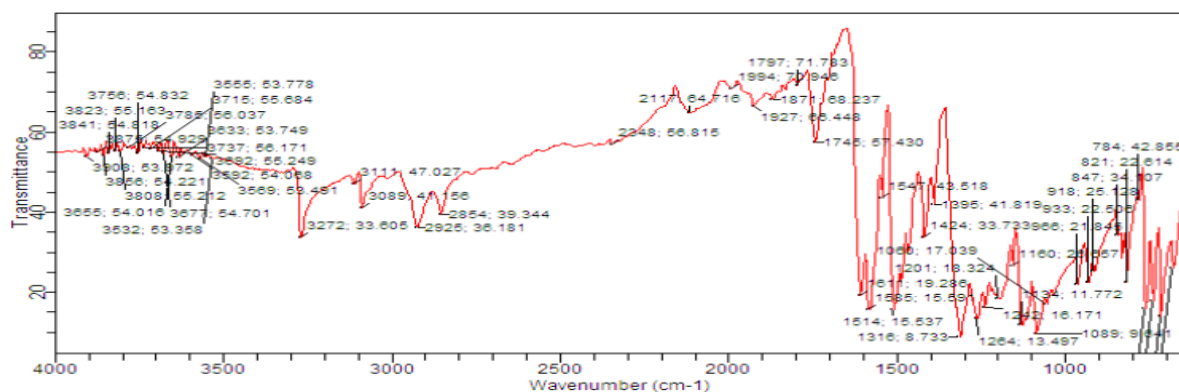


Figure 4: FT-IR spectra of the Mn (II) Complex

RESULTS AND DISCUSSION

Results

The results obtained from various analyses in this research are presented in the following Tables

Table 1: Physical properties of the ligand and its Metal (II) Complex

Compound	Colour	%Yield	M.P/D.T (°C)
Ligand	Pale orange	67	220
Co (II) Complex	Orange	89	250
Mn (II) Complex	Deep Orange	81	246

Table 2: Solubility of the ligand and its Metal (II) Complex in Water and some solvent

Compound	Ligand	Co (II) Complex	Mn (II) Complex
Distilled Water	IS	IS	IS
Ester	IS	IS	IS
Methanol	SS	SS	SS
Ethanol	SS	S	S
Acetone	SS	SS	SS
Dimethylsulfoxide (DMSO)	S	S	S

S= soluble, IS= Insoluble, SS= slightly soluble

Table 3: Magnetic measurement values of the metal (II) complexes

Complexes	$X_g(\text{erg G}^{-2}\text{g}^{-1})$	$X_m(\text{ergG}^{-2}\text{mol}^{-1})$	μ_{eff} (BM)	Property
Co (II) complex	158.80×10^{-7}	7.43×10^{-3}	3.41	Paramagnetic
Mn (II) complex	293.76×10^{-7}	15.55×10^{-3}	5.90	Paramagnetic

Table 4: FT-IR Spectral Data of the Ligand and its Metal (II) Complex

Compound	$\nu(\text{C=N}) \text{ cm}^{-1}$	$\nu(\text{C-O}) \text{ cm}^{-1}$	$\nu(\text{OH}) \text{ cm}^{-1}$	$\nu(\text{M-N}) \text{ cm}^{-1}$
Ligand	1611 cm^{-1}	1201 cm^{-1}	—	—
Co (II) complex	1618 cm^{-1}	1272 cm^{-1}	3339 cm^{-1}	615 cm^{-1}
Mn (II) complex	1514 cm^{-1}	1242 cm^{-1}	3272 cm^{-1}	784 cm^{-1}

Table 5: Conductivity measurement for the Metal (II) complexes

Compounds	Electrical conductance ($\text{ohm}^{-1}\text{cm}^2$)	molar conductance ($\text{ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$)
Co (II) complex	9.2×10^{-6}	9.2
Mn (II) complex	11.1×10^{-6}	11.1

Discussions

The prepared ligand is a solid orange crystal. The obtained manganese (II) and cobalt (II) complexes have decomposition temperatures of 250°C and 246°C, respectively, and are crystalline oranges. The complexes' stability was demonstrated by the high decomposition temperatures. The ligand and its metals (II) complexes were found soluble in most common organic solvents but insoluble in water. The molar conductance measurements (Table 2) of the complexes in 10-3M dimethylsulphoxide (DMSO) is in the range 9.2 – 11.1 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, which are relatively low, indicating non-electrolytic nature. The magnetic susceptibility Measurements (Table 1) provided the magnetic property of the metal complexes. The magnetic moment value of Mn (II) complex is 3.41 BM; whereas that of Co (II) complexes is 5.90. These indicate that, both the metal complexes are paramagnetic. The IR spectra results (Table 3) of the free ligand shows the broad band at 3339 cm^{-1} assigned to $\nu(\text{O-H})$ stretching vibration. The strong peak at 1618 cm^{-1} is attributed to azomethine $\nu(\text{C=N})$ group. The band at 1514 cm^{-1} observed in the metal complexes indicate the participation of the azomethine nitrogen in coordination to the metal ions. Two absorption bands in the range 615-784 in the metal(II) chelates indicate the formation of M-N bonds in the metal (II) ions respectively as shown in Table. The number of coordinated ligands per metal ion was also determined using Jobs method of continuous variation. For each metal (II) complex, absorbance versus mole fraction of the ligand was plotted. The mole fraction of the ligand at maximum absorbance was used in calculating the number of a ligand coordinated to respective metal ions (Mn²⁺, Co²⁺). The results obtained show that the metal to ligand ratio is 1: 2 also as shown in Figs. 1 and 2 respectively. As reported by Raju and Balasubramanian, 2011

(Table 2). The complexes' molar conductance measurements in 10-3M dimethyl sulphoxide (DMSO) are in the range of 9.2 to 11.1 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, which is rather low and suggests that they are not electrolytic in nature (Raju and Balasubramanian, 2011). (Table 1). The magnetic properties

of the metal complexes are determined by the magnetic susceptibility measurements. Mn (II) complex has a magnetic moment value of 3.41 BM. Co (II) complexes have a magnetic moment value of 5.90. These show that both complexes exhibit paramagnetic behavior (Table 3). The free ligand's IR spectra investigation reveals the broad band at 3339 cm^{-1} , which is attributed to the $\nu(\text{O-H})$ stretching vibration. The azomethine $\nu(\text{C=N})$ group is responsible for the prominent peak at 1618 cm^{-1} . The presence of the azomethine nitrogen in the coordination to the metal ions is indicated by the band at 1514 cm^{-1} that has been found in metal complexes.

CONCLUSION

A Schiff base ligand derived from salicylaldehyde and 2,4-dinitrophenylhydrazine and their Mn(II) and Co(II) complexes were synthesized successfully. The FTIR spectral data showed that the Schiff base was coordinated to the metal ions and characterized by melting point/decomposition temperature, solubility, molar conductance, magnetic susceptibility. Characterization showed the complexes to be non-electrolyte with a variable degree of solubility in some common organic solvent. The magnetic moments of the complexes happens to be in the expected range for octahedral complexes. The Schiff base behaves as bidentate ligand and is coordinated to the central metal ion through the azomethines and oxygen from the hydroxyl group. The metal (II) complexes have tetrahedral geometry. The synthesized ligand and its metal(II) complexes were screened and the ligand showed high activity compared to the complexes.

REFERENCES

Ajibade Peter A. and Ikechukwu P. Ejidike., (2015). Synthesis, Characterization and Biological Studies of Metal (II) Complexes of (3E)-3-[(2-((E)-[1-(2,4-Dihydroxyphenyl) ethylidene]amino)ethyl)imino]-1-phenylbutan-1-one Schiff Base. *Journal of Chemical and Pharmaceutical Research*, (ISSN 1420-3049).

- Aliyu, H. Nand Sani, U., (2012). Synthesis, characterization and biological activity of manganese (II), iron (II), cobalt (II), nickel (II) and copper (II) Schiff base complexes against multidrug resistant bacterial and fungal pathogens. *International Research Journal of Pharmacy and Pharmacology*, 2(February), pp.40–44.
- Babu, K. and Amutha, P., (2014). The new Cu (II) and Ni (II) complexes of Schiff bases: Synthesis, characterization and antibacterial studies. *Der Pharma Chemica*, 6(1), pp.432–435.
- Brodowska, K. and Lodyga-Chruscinska, E., (2014). Schiff bases – interesting range of applications in various fields of science. *CHEMIK*, 68(2), pp.132–134.
- Chacrabarti, P., (1993). Synthesis, characterization and antimicrobial studies of Cu (II) complexes with semicarbazone and salicylaldehyde. *Journal of Molecular Biology*, vol 234, p.463. *Polish Journal of Chemistry*, 625(79), pp.619–625.
- Cotton, F.A and Wilkinson, J., (1962). “Advanced Inorganic Chemistry.” *Journal of Advanced Research*, 2nd edition (Interscience Publishers, New York), pp.124–129.
- Fugu, M. B., Ndahi, N.P., Paul, B.B. and Mustapha, A.N., (2013). “Synthesis, characterization, and antimicrobial studies of some vanillin Schiff base metal(II) complexes” *Journal of Chemical and Pharmaceutical Research*, *Journal of synthesis and Reaction in Metal Organic Chemistry*, vol. 5(4), p. pp 22–28.
- Gehad, Ahmed., (2006). Metal Complexes of Schiff Bases Preparation, Characterization, and Biological Activity _ Gehad Ahmed - Academia ., pp.361–382.
- Gopu, P. and Xavier, A., (2015). Synthesis and Characterization of 4- (3-bromo-5- chloro-2-hydroxybenzylidimino) Benzoic Acid and its Transition Metal Complexes. *International Journal of Science and Research(IJSR)*, 4(8), pp.1491–1495.
- Kumar, G., Devi, S. and Johari, R., (2012). Synthesis and Spectral Characterization of Schiff Base Cr (III), Mn (III), and Fe (III) Novel Macrocyclic Complexes Derived from Thio-carbohydrazide and Dicarboxyl Compound. *E-Journal of Chemistry*, 9(4), pp.2255–2260.
- Kumar, N. and Sharma, P., (2013). Synthesis of New Schiff-Base Complexes and Their Applications. *International Journal of Applied Research & Studies*, II(2), pp.1–6.
- Monika, T., and Sulekh, C., (2012). Synthesis, Characterization and Biocidal Properties of Platinum Metal Complexes Derived from 2,6-diacetylpyridine(bis thiosemicarbazone). *open journal of inorganic chemistry*, 3(1), pp.41–48.
- Raju, V.V. and Balasubramanian, K.P. (2011). Synthesis, spectral characterization, catalytic and biological studies of new Ru (II) carbonyl Schiff base complexes of active amines. *Natural Science*, 3(7):542–550.
- Rehman, M., Imran, M. and Arif, M., (2013). Synthesis, Characterization and in vitro Antimicrobial studies of Schiff-bases derived from Acetyl acetone and Amino acids and their Oxovanadium (IV) complexes. *American Journal of Applied Chemistry*, 1(4), pp.59–66.
- Sharma, K., Swami, M., Singh, R., Fahmi, N. and Singh, R. V., (2009). “Coordination chemistry of palladium(II) and Platinum(II) complexes with bioactive Schiff bases: Synthetic, spectral, and biocidal aspects” *Russian Journal of Coordination Chemistry*, *Journal of Advanced Research*, Vol.35(2), pp.142–148.
- Shelar Mahendra Devidas, Shujaat Hussain Quadri, Arjun Kamble, F.M.S. and D.Y.V., (2011). Novel one-pot synthesis of Schiff base compounds derived from different diamine and aromatic aldehyde catalysed by P₂O₅/SiO₂ under free-solvent condition at room temperature. *Journal of Chemical and Pharmaceutical Research*, 3(2), pp.489–495.
- Shushizadeh, M.R. and Azizyan, S., (2014). Solvent-Free Preparation of Novel 2- [Phenyl (Pyridine-2-Yl amino) Methyl] Phenols as Pseudo-Betti Processor for Natural Products. *Jundishapur Journal of Natural Pharmaceutical Production*, 9(4), pp.2–5.
- Silva, J.F.M., Garden, S.J. and Pinto, A.C., (2001). The Chemistry of Isatins : a Review from 1975 to 1992. *Synthesis of Isatins. Journal of Brazilian Chemical Society*, 12(3), pp.273–324.
- Singh, Dharam P. A. L. Grover, Vidhi Kumar, and Krishan Jain, Kiran., 2011. Synthesis and characterization of divalent metal complexes of the macrocyclic ligand derived from isatin and 1,2-diaminobenzene. *Journal of the Serbian Chemical Society*, 76(3), pp.385–393.
- Sonar, A.N., (2011). Acoustic and Volumetric properties of substituted heterocyclic compounds in dioxane-water mixture at 303K. *Journal of Chemical and Pharmaceutical Research*, 3(4), pp.485–489.
- Subramani, P., (2009). Characterisation of nickel (II) Schiff base complexes derived from acetylacetone or salicylaldehyde with tripod amine. *RASAYAN J.Chem*, 2(4), pp.935–936.
- Turki, A.A., Al-hazaam, H. and Abbas, A.F., (2013). Synthesis, Characterization and Computational Study of some New Schiff. *Der Pharma Chemica*, 5(5), pp.307–313.
- Ummathur, M.B., (2007). Metal complexes of Schiff's bases derived from 3- (arylazo) -2, 4- -pentanediones with 2-aminophenol and 2-aminothiophenol having novel structural features and unusual physico-chemical properties. *Journal of the Serbian Chemical Society*, 72(11), pp.1075–1084.
- Usharani, M., (2013). Pharmacological properties of Schiff base metal complexes derived from substituted pyridine and aromatic amine A REVIEW. *International Journal of Pharmaceutical Sciences and Health Care*, 5(3), pp.1–11.
- Vinita, G., Sanchita, S. and Gupta, Y.K., (2013). Synthesis and Antimicrobial Activity of some Salicylaldehyde Schiff bases. *Research Journal of Chemical Sciences*, 3(9), pp.26–29.
- Wadher, S. J. Karande, N. A. Borkar, D. S. and Yeole, P. G., (2009). Synthesis and biological evaluation of Schiff bases of cinchophen as antimicrobial agents. *International Journal of ChemTech Research*, 1(4), pp.1297–1302.
- Maurya RC, Verma R, Singh H., (2003). Synthesis and Physico-Chemical Studies of Some Mixed-Ligand Complexes of bis (Benzoylacetato)copper(II) with Some Biologically Active Heterocyclic Chelating Donors. *Synthesis and Reactivity in Inorganic and Metalorganic Chemistry*, 33(6): 1063-1080

