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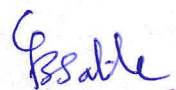
**Department of Chemistry**


**MoU Activity Report**

Following activity was conducted between Devrukh Shikshan Prasarak Mandal's (DSPM's) Nyayadhish Tatyasaheb Athalye Arts, Vedmurti S.R. Sapre Commerce and Vidhidnya Dadasaheb Pitre Science College, (Autonomous) Devrukh and Dapoli Urban Bank Senior Science College, Dapoli, Dist. Ratnagiri, Maharashtra under the Memorandum of Understanding (MoU) signed by two Principals on 14<sup>th</sup> June, 2019.

Name of Activity: - **Research Collaboration.**

1. Dr. G. B. Sathe, Mr. S. S. Marathe and Mr. M. L. Lad, Department of Chemistry and Dr. S. T. Sankpal, Head of Department of Chemistry have published joint research paper titled "Synthesis and Characterization of Novel Manganese(II), Cobalt(II) and Nickel(II) Schiff bases complexes of Salen ligand".

  
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## Synthesis and characterization of Novel Manganese (II), Cobalt (II) and Nickel (II) Schiff bases Complexes of Salen ligand

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### Abstract

**Objectives:** Schiff base metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas.

**Methods:** Biologically Active C<sub>2</sub>-symmetric salen base 2-[(E)-N-(2-{[2-(E)-[(2-hydroxyphenyl)methylidene] amino] phenyl} (methyl amino) phenyl} carboximidoyl] phenol (HHMCP) have been synthesized. Metal Chelates of HHMCP Manganese (II), Cobalt (II) and Nickel (II) metals have been synthesized and the structures of these chelates have been elucidated by elemental analysis, IR spectroscopy, electronic spectral data, conductometry, Thermogravimetry (TGA) and magnetic susceptibility measurements. **Findings:** The chelate of Mn (II) and Ni (II) appears to be octahedral and Co (II) appears to be tetrahedral geometry.

**Findings:** From these studies it is found that the ligands HHMCP act as hexadentate ligand coordinating through oxygen and nitrogen donor atoms.

**Key words:** C<sub>2</sub>-symmetric salen, Schiff bases, metal chelate, HHMCP, Salen base.

### Introduction

Metal Complexes of schiff bases have occupied central place in the development of coordination chemistry after the work of Jorgensen and Werner. Etling isolated a dark green crystalline product from the reaction of cupric acetate, salicylaldehyde and aqueous ammonia. Schiff prepared 1:2 complexes of metal salicylaldehyde and primary amines. Subsequently, Schiff prepared complexes by allowing metal acetate, salicylaldehyde and a primary amine to react in alcohol and demonstrated a 2:1 stoichiometry. A systematic synthetic study of schiff base complexes was commenced by Pfeiffer and coworkers. Prior to this it was revealed that transition metal ions formed coloured reaction products with a variety of schiff bases derived from substituted salicylaldehyde. Then Dubsky and Sokol isolated N, N-bisalicylidinediamine copper (II) and Nickel (II) complexes and identified their structures. Latter Pfeiffer and his coworkers produced a classic series of papers on a variety of complexes derived from Schiff Bases of salicylaldehyde and its substituted products.

In many catalytic applications Schiff base metal complexes are prepared in situ by producing a reaction between the Schiff base and available and well-defined metal complexes. This approach is clearly simple and suitable for catalytic applications. Essentially, five different synthetic routes can be identified for the preparation of Schiff base metal complexes.<sup>[1]</sup>

Route 1 involves the use of metal alkoxides (M(OR)<sub>n</sub>). The reaction of a Schiff base with a metal alkoxide is an equilibrium reaction and the identity of the species generated is sometimes difficult to predict. Metal amides M(NMe<sub>2</sub>)<sub>4</sub> (M ~ Ti, Zr) are also highly suitable precursors for the preparation of Schiff base metal complexes of early transition metals (Route 2). The reaction occurs via the elimination of the acidic phenolic proton of the Schiff bases, occurring at the same time as the formation of volatile NHMe<sub>2</sub>. A Schiff base metal complex can be prepared in a clean and effective way using metal alkyl complexes as precursors (Route 3). Many Schiff base metal complexes can be obtained through the treatment of the Schiff base with the corresponding metal acetate, normally by heating the Schiff base in the presence of the metal salt under reflux conditions (Route 4). The synthetic scheme presented in route 5 is quite effective in obtaining Salen metal complexes. It consists

of a two-step reaction involving the deprotonation of the Schiff bases and a successive reaction with metal halides.

When large amounts of Salens are available, performing the synthesis on a large scale could be recommended using route 5. Generally, the formation of the Salen metal complex via route 5 is performed in THF and the insoluble sodium or potassium halides obtained as by-products can be eliminated by filtration. However, as the oxygens of the M(Salen) are Lewis basic centers, coordination of sodium or potassium halides could result, leading to many problems in the purification of the Schiff base metal complexes. For catalytic purposes, when synthesis is performed in situ by route 5, the presence of coordinated salts can alter the catalytic performance of the Schiff base metal complexes.

In the present work, *C*<sub>2</sub>-symmetric salen type schiff base 2-[(E)-N-(2-[[2-[(E)-[(2-hydroxyphenyl)methylidene] amino] phenyl] (methyl amino) phenyl] carboximidoyl] phenol (HHMCP)<sup>[2]</sup>, (10<sup>-2</sup> M) was prepared and treated with metal salts to give complexes.

The reagent was successfully used in spectrophotometric determination of Ni (II)<sup>[3]</sup>, Pd (II)<sup>[4]</sup>, and Ru (III)<sup>[5]</sup>,

### Materials and methods

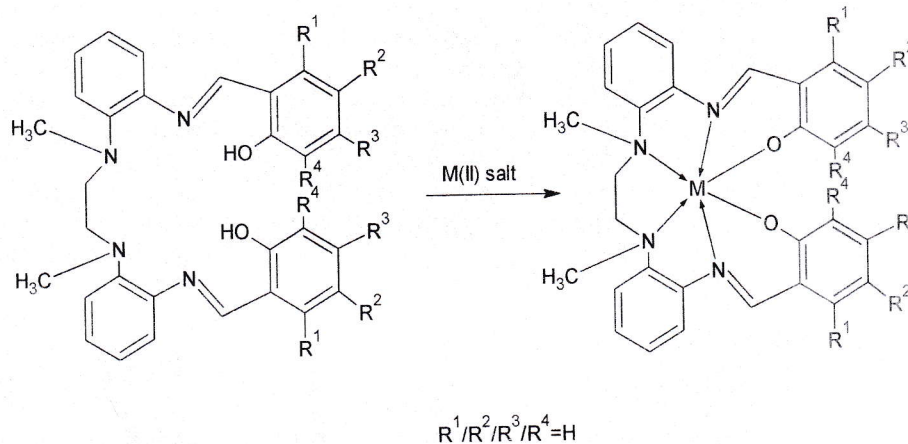
All reagents used were obtained from Aldrich, S. d. Fine and loba chemicals and are chemically pure or analytical reagent grade. All metal salts (II) were used as chlorides. The solvents used in the present investigation are acetone, dichloromethane, chloroform, petroleum ether; ethanol & DMF were obtained from sd-fine and were purified and dried by conventional methods.<sup>[6]</sup>

Infrared spectra were measured in KBr pellets on a Nicolet Instruments Corporation, USA Model MAGMA-550 (4000-50 cm<sup>-1</sup>) from IIT Mumbai. UV visible spectra were obtained in DMF on systronics 2201 double beam spectrophotometer. Room temperature magnetic measurements were made on solid complexes by Gouy method using Hg [Co (SCN)<sub>4</sub>] as the calibrant. The molar conductance values at room temperature were measured in nitrobenzene on Equip-tronics digital conductivity meter model EQ-661A. Thermogravimetric data were obtained on Perkin Elmer (USA), model Diamond TG/TGA with heating rate of 10<sup>0</sup>C min<sup>-1</sup>.

### General Procedure for Synthesis of Schiff base Complexes:

The Schiff base complexes were prepared by mixing methanolic solution of GBS 3a (HHMCP) with the methanolic solution of NiCl<sub>2</sub>·6H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, MnCl<sub>2</sub>·4H<sub>2</sub>O. Few drops of ammonium hydroxide were added to adjust the PH. The obtained mixture was refluxed for about 4 hours. The resulting products were filtered, collected and the washed with alcohol until the filtrate becomes clear. Yields: above 70%

All the complexes are intense coloured, thermally stable at room temperature, non- hygroscopic, and show low solubility in common organic solvents but sparingly soluble in DMF. The analytical data for ligands and complexes are consistent with proposed structures and indicate that the complexes have 1:1 metal-ligand stoichiometry. All the complexes prepared have been found to be biologically active.<sup>[7]</sup>





## Scheme : Preparation of Schiff base complexes..

### Results and Discussion

#### *Physical Properties:*

The analytical data for ligands and complexes are consistent with proposed structures and indicate that the complexes have 1:1 metal-ligand stoichiometry. The structural formulae were confirmed by spectral techniques with results in good agreements with projected compounds. The microanalysis, molecular formula, percentage yield, decomposition temperature and molar conductivity data of all the complexes are summarized in Table 1 & 2. The microanalysis data of the complexes are consistent with their calculated results obtained from the empirical formula of each compound. The melting/decomposition points were determined in house by placing a finely powered sample in a glass capillary and heating by using Barnstead/electrothermal digital melting point apparatus and are uncorrected.

#### *Elemental analyses:*

The carbon, hydrogen, nitrogen and metal content provide correct picture about the molecular formula as well as the purity of the compounds. Carbon, hydrogen and nitrogen content of the complexes were estimated on a Thermo Finnegan FLASH EA-112 CHNS analyzer at IIT, Mumbai. The analytical data indicate that the observed C, H, N values of the complexes were in close agreement with that of the formula suggested. Metal contents of the complexes were estimated after decomposing the complexes with 1:1 mixture of conc. nitric acid and perchloric acid. The solution was evaporated repeatedly and the residue was extracted with dilute hydrochloric acid and water. The amounts of metal ion in the solution obtained were determined by standard method<sup>[6]</sup> & later confirmed by AAS after digestion with conc. HNO<sub>3</sub> and was found to be consistent with that of the theoretical results.

#### *Molar Conductivity:*

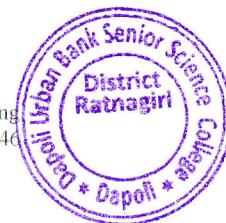
The measurement of molar conductance is an important tool that gives valuable information about the coordination number, structure of the complexes and the nature of counter ions present in the complexes. It also helps to confirm the electrolytic nature and thereby the number of ions present outside the coordination sphere.

The molar conductance of all the complexes was measured at room temperature in nitrobenzene solution (10<sup>-3</sup> M) and the results are summarized in Table 2. In nitrobenzene solution all the complexes show molar conductivity values in the range of 23-30 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. These results indicate that, although some dissociation of these complexes seems to occur in the solvent, the conductance values support the non-electrolytic nature of all the complexes, This is further supported by proposed general formulae of the complexes as suggested depending upon the results of the microanalysis and IR spectra.

#### *Magnetic moment:*

The magnetic moment measurements of the complexes can be used to draw inferences about the stereochemical configurations. In conjunction with electronic spectra it can be used to draw the proposed structure of the complexes. The magnetic susceptibility of polycrystalline complexes were measured by using Gouy method at room temperature. Hg[Co(SCN)<sub>4</sub>] with a magnetic susceptibility of 1.644 X 10<sup>-5</sup> cm<sup>3</sup>/g, was employed as a calibrant. The correction of diamagnetism of the constituents of atoms was calculated using Pascal's constant. The effective magnetic moments (μ<sub>eff</sub>) of all the complexes were calculated from the room temperature magnetic susceptibility measurements (χ<sub>g</sub>) and the results are summarized in Table 2.

The magnetic moment values of *HHMCP* - Ni complex is found to be 2.88. The room temperature magnetic moments for octahedral Ni (II) complexes d<sup>8</sup>(t<sub>2g</sub><sup>6</sup> eg<sup>2</sup>) are usually found in the range of 2.9-3.3 μB and are temperature dependent. The magnetic moment of *HHMCP*-Mn(II) complexes are found to be 5.22. From these values it can be concluded that these complexes are octahedral d<sup>5</sup> high spin (t<sub>2g</sub><sup>3</sup> eg<sup>2</sup>) complexes. The magnetic moment values of *HHMCP* -Co (II) complexes are found to be 4.0. The room temperature magnetic moments for octahedral Co (II) complexes d<sup>7</sup> (t<sub>2g</sub><sup>5</sup> eg<sup>2</sup>) are usually found in the range of 4.3-5.2 μB and are temperature dependent.



**Table 1: Analytical, Magnetic moment and electronic spectral data of M (II) complexes**

Compound	Yield (%)	M. P. (°C)	Magnetic Moment ( $\mu_{\text{eff}}$ )	n- $\pi^*$ and $\pi$ - $\pi^*$ & Charge transfer transitions (cm <sup>-1</sup> )	d-d transitions (cm <sup>-1</sup> )
HHMCP -Ni	72	261	2.88	35335 28571 23094 20120	16778 15432
HHMCP -Mn	70	232	5.22	28571 20242	16778
HHMCP -Co	79	233	4.01	28571 21645 20120	16778

**Table 2: Analytical & Physicochemical Data of the Schiff Base complexes**

Compound	M. F.	Elemental Analysis, % found (Calculated)				Molar Conductance (Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	$\mu_{\text{eff}}$ (B.M.)
		M	C	H	N		
HHMCP -Ni	C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>2</sub> Ni	10.67 (11.02)	67.50 (67.28)	5.16 (5.23)	10.63 (10.46)	23	2.88
HHMCP -Mn	C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>2</sub> Mn	10.21 (10.35)	67.61 (67.79)	5.12 (5.27)	10.66 (10.54)	30	5.22
HHMCP -Co	C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>2</sub> Co	10.88 (11.02)	67.11 (67.28)	5.45 (5.23)	10.59 (10.46)	24	4.01

**Electronic spectra of the metal(II) complexes:**

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The electronic spectral measurements were used for assigning the stereochemistry of metal complexes based on the positions and number of *d-d* transition peaks. The electronic absorption spectra of metal(II) complexes with *HHMCP* were recorded in 10<sup>-3</sup> M to 10<sup>-5</sup> M solutions of each complex in DMF and chloroform in the range 200–1100 nm at room temperature.. The results of the solution spectra are presented in Table 1.

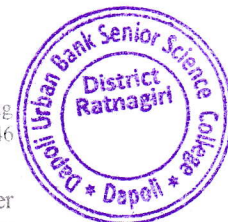
For the Nickel (II) complex of *HHMCP* exhibits bands at 35335, 28571, 23094 & 20120 cm<sup>-1</sup> can be assigned to intra-ligand & charge transfer transitions. The Mn(II) complex of *HHMCP* exhibits bands at 28571, 20242 & 16778 cm<sup>-1</sup>. The bands observed at 28571 & 20242 can be assigned to intra-ligand & charge transfer transitions. The Co(II) complex *HHMCP* showed bands at 28571, 21645, 20120 & 16778 cm<sup>-1</sup>. The bands observed at 28571, 21645 & 20120 can be assigned to charge transfer transitions (MLCT) & intra-ligand transitions.

Thus electronic spectrum of complexes is in agreement with the magnetic moment values which suggest octahedral geometry for the complexes.

**Infrared spectra:**

The IR spectra of the free Schiff base were compared with their respective metal complexes in order to determine the coordination mode of the ligands.

The ligand *HHMCP* show an intense band at 1616 cm<sup>-1</sup> assigned to the azomethine,  $\nu$  (HC=N) linkage. In all the metal complexes this band undergoes shift to lower frequency by about 5-16 cm<sup>-1</sup>. The  $\nu$  (C=N) stretching bands are thus strongly affected by chelation and are shifted to lower wavenumbers which is attributed to the conjugation of the *p*-orbital on the double bond with the *d*-orbital on the metal ion with the reduction of the force constant<sup>[8]</sup>. This supports the participation of imine group of the azomethine in binding to the metal ion.



The azomethine vibration of ligand *HHMCP* at  $1616\text{cm}^{-1}$  was shifted to lower frequencies after complexation, appearing at 1611, 1604 and  $1610\text{cm}^{-1}$  for Ni (II), Mn (II) and Co(II) complexes respectively. The medium intense and broad band in the range 2300-3500 shows the existence of strong intramolecular H-bonding between phenolic oxygen and azomethine nitrogen (O---H---N)<sup>[9]</sup>. This band is absent in the spectra of complexes indicating that phenolic -OH groups are deprotonated. The presence of strong band at 1149 in Schiff base 3a is a typical of phenolic C-O stretching which showed marked shift to lower wave number in the complexes. These bands appeared at 1144, 1139 and 1140 for Ni (II), Mn (II) and Co (II) complexes respectively indicating metal-Oxygen bonding.<sup>[10]</sup> Thus, it can be concluded that the Schiff bases acted as hexadentate ligand & coordinated via the azomethine N and the phenolic O.

**Table 3: Infrared absorption Frequencies of 3a-M (II) Complexes ( $\text{cm}^{-1}$ )**

Compound	IR Frequencies ( $\text{cm}^{-1}$ ) with tentative assignments
HHMCP (Schiff base)	3500-2300 broad $\nu(\text{Ar-OH})$ , 3057 $\nu(\text{Ar-H})$ , 2999 & 2966 $\nu(\text{CH}_2 \text{ \& \ } \text{CH}_3)$ , 1616 $\nu(\text{C=N})$ , 1587 & 1566 $\nu(\text{C=C})$ , 1166 $\nu(\text{C-O})$ .
HHMCP -Ni	3056 $\nu(\text{Ar-H})$ , 2962 & 2923 $\nu(\text{CH}_2 \text{ \& \ } \text{CH}_3)$ , 1611 $\nu(\text{C=N})$ , 1522 & 1492 $\nu(\text{C=C})$ , 1144 $\nu(\text{C-O})$ .
HHMCP -Mn	3060, 3034 $\nu(\text{Ar-H})$ , 2970 $\nu(\text{CH}_2 \text{ \& \ } \text{CH}_3)$ , 1604 $\nu(\text{C=N})$ , 1526 & 1491 $\nu(\text{C=C})$ , 1139 $\nu(\text{C-O})$ .
HHMCP -Co	1600 $\nu(\text{C=N})$ , 1578, 1524 & 1493 $\nu(\text{C=C})$ , 1140 $\nu(\text{C-O})$ .

#### Thermo Gravimetric Analysis:

Thermal decomposition studies were made by heating the complexes to increasing temperatures starting from room temperature with heating rate  $10\text{ }^\circ\text{C min}^{-1}$ . The decomposition temperatures ( $>300\text{ }^\circ\text{C}$ ) of the chelates indicates that they are thermally stable suggesting stronger metal-ligand bonding. The thermal curves of metal complexes are single stepped, indicating gradual decomposition of ligand after the decomposition point, leaving metal (II) oxide as the ultimate products. It also supports the absence of water molecules in the complexes, which further supports the IR spectral studies.

#### Conclusion

The analytical data for ligands and complexes are consistent with proposed structures and indicate that the complexes have 1:1 metal-ligand stoichiometry. The chelate of Mn (II) and Ni (II) appears to be octahedral and Co (II) appears to be tetrahedral geometry. From these studies it is found that the ligands *HHMCP* act as hexadentate ligand coordinating through oxygen and nitrogen donor atoms.

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