Final Report

for

UGC Sponsored

Minor Research Project

"Synthesis of Schiff's Bases of Substituted Acetophenones and determination of metal ligand stability constant by different analytical techniques"

Submitted to

PSGVP Mandal's ASC College,
Shahada 425 409 Dist. Nandurbar

Submitted by

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(2012)

Annexure -III

UNIVERSITY GRANTS COMMISSION

BAHADUR SHAH ZAFAR MARG

NEW DELHI – 110 002 .

Final Report of the work done on the Minor Research Project.

1. Project report No. : Final
2. UGC Reference No. : No F. 47 – 828 / 09 (WRO) dated 2-09-2009.
3. Period of report : 1st October 2009 to 31st March 2012.
4. Title of research project : "Synthesis of Schiff's Bases of Substituted Acetophenones and determination of metal ligand stability constant by different analytical techniques"
5. (a) Name of the Principal Investigator : Shri. S. B. Patil

   (b) Dept. And University / college where work has progressed:

   Dept. of Chemistry, P.S.G.V.P. Mandal's SIP Arts, GBP Science & STSKVS Commerce College, Shahada, PIN- 425 409, Dist. Nandurbar (Maharashtra).
6. Effective date of starting of the project : 01.10.2009
7. Grant approved and expenditure incurred during the period of the report:

a. Total amount approved : Rs.1,43,000 /-

b. Total expenditure : Rs. 1,44,128/-

c. Report of the work done : (Please attach a separate sheet)

(i) Brief objective of the project: **Annexure III a**

(ii) Work done so far and results achieved and publications, if any, resulting from the work (Give details of the papers and names of the journals in which it has been published or accepted for publication): **Annexure III b**

(iii) Has the progress been according to original plan of work and towards achieving the objective. If not, state reasons : Yes, the progress has been satisfactory and according to original plan.

(iv) Please indicate the difficulties, if any, experienced in implementing the project: No difficulties were experienced in implementing the project. The support extended by college has been satisfactory.

(v) If project has not been completed, please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the Commission on a separate sheet: Summary of the work done for the period is given in **Annexure III c**.

(vi) If the project has been completed, please enclose a summary of the findings of the study. Two bound copies of the final report of work done may also be sent to the Commission: Final report of the work done is submitted herewith.

(vii) Any other information which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as (a) Manpower trained: Nil

(b) Ph. D awarded : Nil

(c) Publication of results: One paper has been accepted for publication

(d) other impact, if any: Nil

(Shri. S. B. Patil)

PRINCIPAL INVESTIGATOR

(Dr. Vishwas K. Patil)

Principal

S. T. S. K. V. S. Commerce College,

Khanapur (Dist. Nanded) M. S.

Annexure III a

Brief objective of the project

Schiff bases have attracted much attention due to their antiviral (1), anticancer (2, 3) antimicrobial (4) and antibacterial (5) activities. Anticancer Schiff bases have been synthesised by condensation of aniline with substituted benzaldehyde (6) Schiff bases like flavones imines have been reported to exhibit antimicrobial properties (7).

Intramolecular hydrogen bonding between -OH hydrogen and -C=N nitrogen atoms of Schiff bases determines the properties of various molecular systems and plays a significant role in many biochemical mechanisms (8). Also, -C=N linkage in the azomethine derivatives is essential for biological activity (9). Since proton transfer is known to be crucial for physicochemical properties and practical application of Schiff bases, this process has been widely studied in literature (10). On the other hand, Schiff bases have been extensively used as ligands in coordination chemistry because of their excellent donor abilities and chelating agents (11-16). Schiff bases metal complexes have many industrial uses, especially in catalysis (17-19), dying and analytical reagents (20-22).

In this study, we synthesized five Schiff bases derived from 3- substituted 2-hydroxy-5-methyl acetophenone and various substituted anilines (Scheme 1). Their application as ligands with metals like Cu(II), Ni(II) and Co(II).

Work done so far and results achieved

The reagents (Hi-Media, Loba) were used as supplied while the solvents were purified according to standard procedures. Melting points were determined in open capillaries and are corrected. Infrared and far-infrared spectra were recorded on a Perkin-Elmer Spectrum GX FT IR System spectrophotometer using KBr pellets (4000–400 cm^{-1}) and nujol mulls dispersed between polyethylene disks (400–40 cm^{-1}). The ^1H, NMR spectra were recorded on a Bruker AC-300 MHz spectrometer. The spectra were acquired at room temperature (298 K). The chemical shifts are reported in ppm with respect to the references (external tetramethylsilane (TMS) for ^1H).

Preparation of the Schiff base:

To the hot stirred solution of 3-substituted 2-hydroxy-5-methyl acetophenone (0.01 mole) in ethanol (30-40 ml) were added substituted aniline (0.01 mole) 2-3 drops of conc. H_2SO_4. The reaction mixture was refluxed for two hours. The resulting mixture was cooled at room temperature. The solid form on cooling was filtered, washed several times with ethanol and dried in a desiccators over calcium hydroxide. The yield of the reaction was 72% given in table 1.

Preparation of the complexes

Complexes of Co(II), Cu(II) and Ni(II) with Schiff base of 3-substituted 2-hydroxy-5-methyl acetophenone were synthesized by mixing ethanolic solutions (50 mL) of 0.02 mole of the synthesized Schiff base with an ethanolic solution (50 mL) of the 0.01 mol of $CoCl_2.6H_2O$, $CuCl_2.2H_2O$ or $NiCl_2.6H_2O$ salts respectively. A few drops of ammonia solution was added to adjust the pH until the complexes isolated. The reaction mixtures were refluxed for three hours and left to cool and filtered by suction. The precipitates were washed several times with ethanol and then with ether. The complexes were dried in desiccators over anhydrous calcium chloride. The yields were 75 and 78% respectively.

(I a-b) (II a-e)

IR Spectra

The IR spectra of the Schiff bases under study are recorded in the solid state using the KBr disc technique. Selected bands of diagnostic importance are collected. The spectra of compounds IIa – IIe having free -OH groups display somewhat broadened bands within the 3434-3425 cm^{-1} region. The presence of –OH groups involved in intramolecular hydrogen bonding for IIa – IIe give the -OH as a shallow, very broad band extending within the 3100-2700 cm^{-1} region. The stretching vibrations of the aromatic C-H groups give medium to weak bands within the range 3072-3043 cm^{-1}. The C=N bands are observed at 1645-1557 cm^{-1}; the position of these bands varies with the molecular structure, though no regularity can be pointed out. The spectra of all compounds show medium to sharp bands within the range 870-630 cm-1 due to the out-of-plane deformations of the aromatic C-H groups.

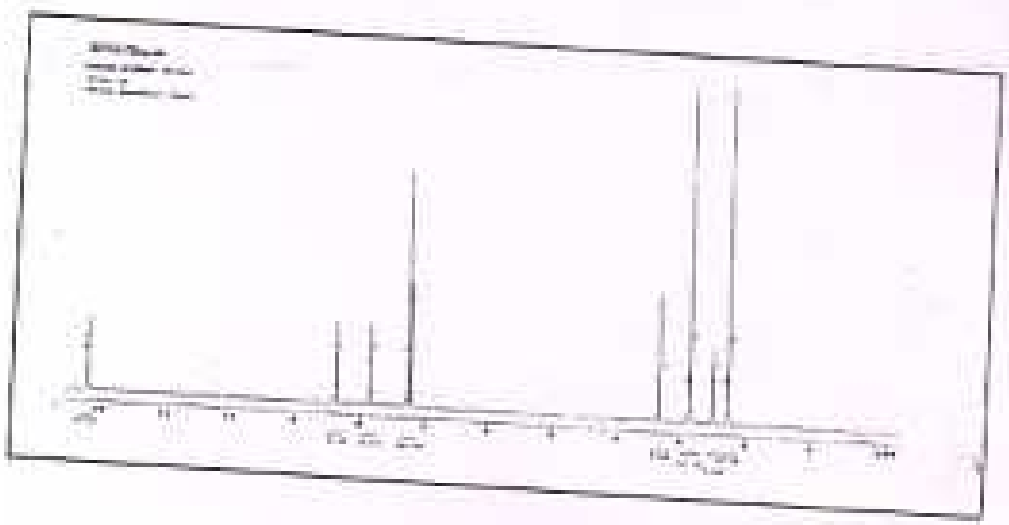
^{1}H NMR:

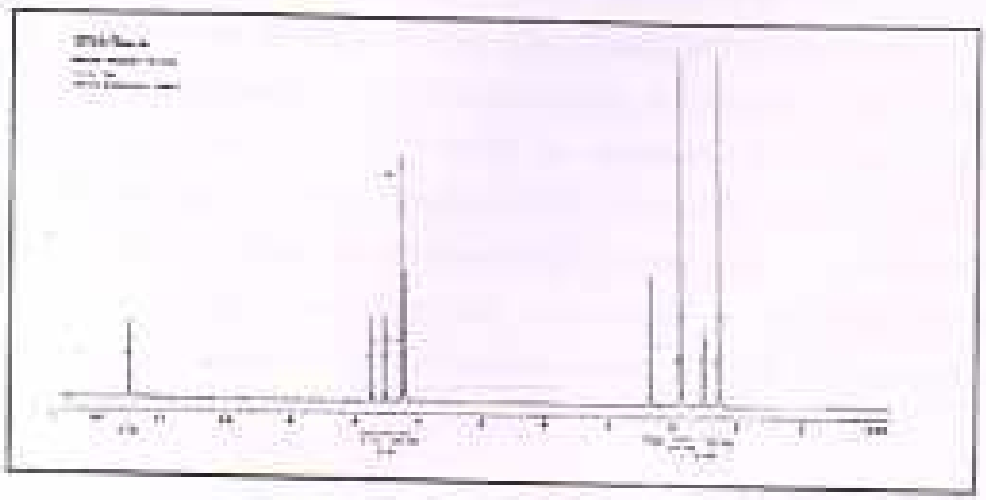
A series of substituted phenoxy-ketimine ligands were synthesized (IIa-IIe). Specifically, the condensation reaction of substituted o-hydroxyacetophenone with the respective anilines in presence of a catalytic amount of H_2SO_4 gave the substituted phenoxy-ketimine ligands (IIa-IIe) in high yield (Scheme 1). The compounds (IIa-IIe) have been characterized by 1H NMR and IR, spectrometry. The signals observed in the 1H NMR spectra of the Schiff bases under study (Figs. 1 to 5). The 1H NMR spectra of (IIa-IIe) showed the ketimine methyl (MeC=N-) resonances as singlets at 2.75–3.00 ppm, while the phenolic –OH protons appeared as broad peaks at 11.5–12.8 ppm. The substantially high downfield shifts of the phenolic –OH protons in (IIa-IIe) are attributed to an intramolecular hydrogen bonding interaction, phenolic –OH. The spectra exhibit a multiplet at 6.59-8.18 ppm for the hydrogens of the aromatic rings as given in table 1.

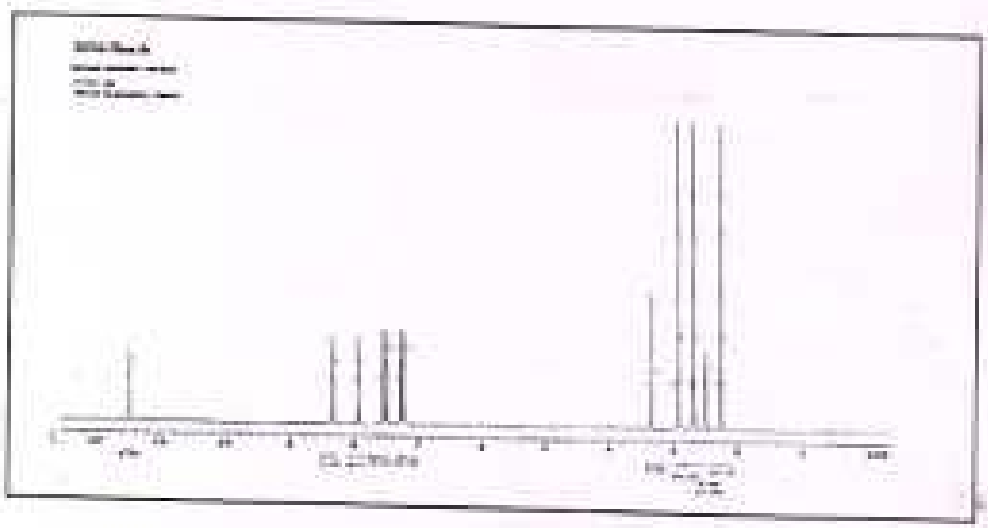
The metal chelates of compound A and B with ions Cu^{2+}, Ni^{2+} and Co^{2+} vary in colors as given below. When compound IIa-IIe is treated with $CuCl_2.6H_2O$, yellow color changes to dirty green. This indicates formation of complex. Similarly compound IIa-IIe treated with $NiCl_2.6H_2O$ and $CoCl_2.6H_2O$, yellow colors changes to light yellow and pale green color respectively.

Table 1. The analytical, physical properties and 1H-NMR spectral data of the compounds **IIa-e**.

Compound No.	R1	R2	R3	R4	Melting points/ °C	% Yield	1H NMR (DMSO-d6, d, ppm)
II a	NO_2	H	H	H	122	85	12.2 (1H, s, -OH), 8.4 (1H, s, ArH), 7.8 (1H, s, ArH), 7.2 (5H, m, ArH), 3.9 (3H, s, -CH3), 2.3 (3H, s, -CH3)
II b	NO_2	NO_2	H	H	103	79	12.2 (1H, s, -OH), 8.3 (1H, s, ArH), 8.1 (1H, s, ArH), 7.8-7.2 (5H, m, ArH), 3.9 (3H, s, -CH3), 2.3 (3H, s, -CH3)
II c	NO_2	H	H	CH_3	204	89	12.2 (1H, s, -OH), 8.3 (1H, s, ArH), 7.9 (1H, s, ArH), 7.5 (2H, d, ArH), 7.3 (2H, d, ArH)
II d	Br	H	H	H	79	83	11.5 (1H, s, -OH), 7.8 (1H, s, ArH), 7.5 (1H, s, ArH), 7.2 (5H, m, ArH), 3.9 (3H, s, -CH3), 2.3 (3H, s, -CH3)
II e	Br	H	H	CH_3	66	86	11.5 (1H, s, -OH), 8.3 (1H, s, ArH), 8.0 (1H, s, ArH), 7.5 (2H, d, ArH), 7.3 (2H, d, ArH) 3.9 (3H, s, -CH3), 2.7 (3H, s, -CH3), 2.3 (3H, s, -CH3)







Annexure III c

Summary of Work done

The present work describes the synthesis of Schiff bases and metal complexes of 2-hydroxy-5-methyl acetophenone derivatives. Three Schiff-Base complexes of Cu(II), Co(II) and Ni(II) were synthesized and Schiff-bases (ligand) was formed by the 1:2 molar. All ligands are characterized by IR and ^1H NMR. The synthesized Schiff bases (Ligand) were found be bidentate ligands. Cu(II), Co(II) and Ni(II) coordinates with the ligand through a oxygen of the phenoxyl group and a nitrogen of C=N azomethine of one molecule of Schiff base.All the synthesized compounds were characterized by performing the IR,NMR spectroscopy.The biological activities of the synthesized compounds was also performed.

(Shri. S. B. Patil)

Principal Investigator