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The new Cu(II) and Ni(II) complexes of schiff bases: Synthesis, characterization and antibacterial studies

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ABSTRACT

We synthesized new schiff bases by the reaction between methyl substituted o-phenylenediamine, 2-OH-naphthaldehyde and isatin. The obtained schiff bases were treated with metal acetates in ethanol medium afforded corresponding metal complexes and these were characterized with help of melting point, molar conductance, UV-Vis, IR, ^{1}HNMR and ^{13}CNMR spectroscopic techniques. Antibacterial activities of newly synthesized compounds were carried out against E. coli (gram negative) and S. aureus (gram positive) bacteria. The transition metal complexes showed good antibacterial activity than the free ligand against selective bacteria were reported.

Keywords: Antibacterial activity, methyl substituted *o*-phenylenediamie, isatin, schiff base,

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INTRODUCTION

Schiff bases are condensation products of primary amines with carbonyl compounds and they were first reported by schiff in 1864. Several studies [1-3] showed that the presence of a lone pair of electrons in sp^2 hybridized orbital of nitrogen atom of the azomethine group is considerable chemical and biological importance. The chemistry of the carbon-nitrogen double bond based complexes plays a vital role in the progresses of chemistry and they have been found to posses the pharmacological activities such as anti-malarial [4], anticancer[5], antibacterial[6-7], antifungal[8-9] anti-tubercular[10-11] antimicrobial[12], anthelmintic[13], and anti-inflammatory activities[14]. Generally schiff bases were obtained by the condensation reaction between amine and carbonyl compounds under reflux condition catalyzed by acid or base. Recently some alternative methods are developed such as microwave irradiation [15], sonication and ultraviolet irradiation [16]. Here in we reported synthesis of new schiff bases, their metal complexes and antibacterial activities of all the synthesized compounds.

MATERIALS AND METHODS

All the reagents and solvents used were of laboratory grade and melting point was determined in open capillaries and is uncorrected. The purity of synthesized compounds were checked by TLC using silica gel G and the spot was visualized in iodine chamber. The IR spectra were recorded on a FT-IR 8400 PERKIN-ELMER 883 spectrophotometer by using KBr pellet. The NMR spectra were recorded on a BRUKER-500 MHz spectrometer in $CDCl_3$ solvent and TMS as an internal standard. The antibacterial activities of both ligand and its metal complexes were studied by disc diffusion method against Escherichia coli, (gram negative), Staphylococcus aureus, (gram positive) bacteria.

Synthesis of schiff bases

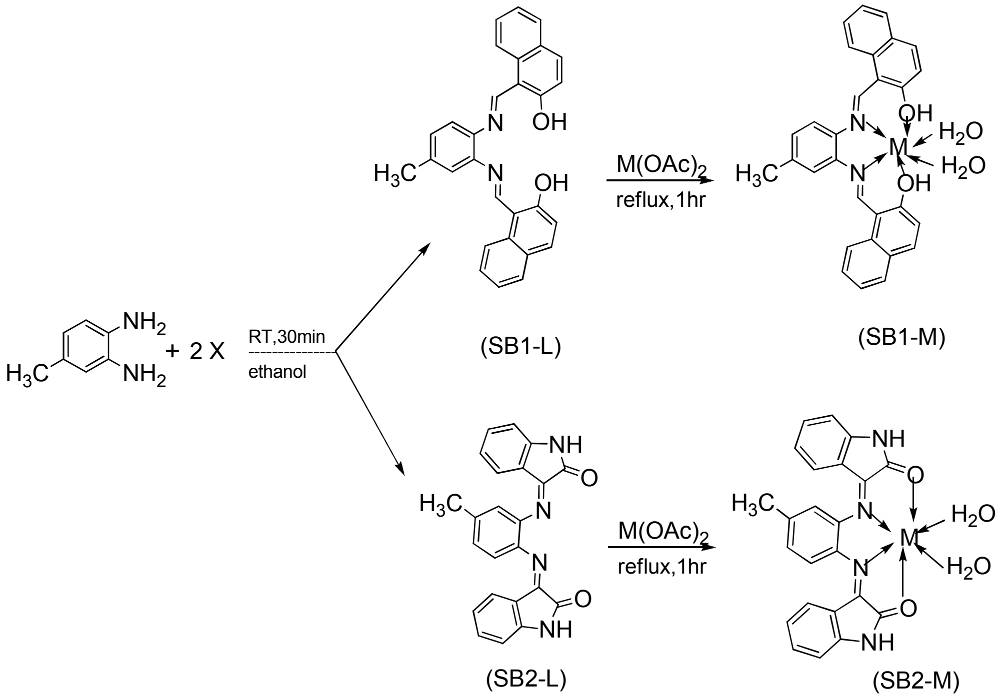
The mixture of aldehyde/isatin and methyl substituted *o*-phenylenediamine were taken in 2:1 molar ratio in distilled water or ethanol which was stirred by using magnetic stirrer at room temperature for desired time (30-45min) afforded corresponding schiff bases. After completion of reaction, the solid formed was filtered and recrystalyzed from ethanol-water mixture (7:3). The reaction was monitored with help of TLC by using 7:3 hexane and ethyl acetate.

Synthesis of complexes

The hot ethanol solution of metal acetates (1 equivalent) was slowly mixed with hot ethanol solution of the respective ligand (1 equivalent) with two drop of sodium hydroxide. The mixture was refluxed for 1-2 hours at 60-70^{o}C and on cooling the contents, the colored complex separated out in each case. It was filtered, washed with ethanol and finally dried.

RESULTS AND DISCUSSION

The one equivalent of 4-Me-1,2-diaminobenze and two equivalent of carbonyl compounds react together in water or ethanol medium at room temperature for 30-45mins produced corresponding bis-schiff bases. The formed schiff bases and metal acetates are refluxed in ethanol medium for 1-2 hour produced metal complexes (Scheme-1)



When X= 2-OH-naphthaldehyde, compound SB1-L obtained

When X= Isatn, compound SB2-L obtained

M=Cu^{2+} and N^{i2+}

Scheme-1: Synthetic pathway of schiff bases and their complexes

The synthesized schiff bases were obtained 70-75% and all the complexes were obtained 50-57%. The detailed physical data such as color, melting point, molar conductance and yield are given in table-1

Table-1: Physical data of schiff bases and their metal complexes

Code	Yield (%)	Mp (°C)	Color	M. conductance ($\Omega^{-1}cm^{2}mol^{-1}$in 10^{-3})
SB1-L	70	165-167	Yellow	---
SB1-Cu	57	<270	Dark brown	201
SB1-Ni	48	<270	Light brown	220
SB2-L	75	135-140	Orange	---
SB2-Cu	52	<270	Dark brown	210
SB2-Ni	50	<270	Light brown	228

Molar conductance:

The metal complexes are soluble in DMSO, DMF, and $CHCl_3$. The molar conductance values measured in DMF solution and the values of all the synthesized complexes are fall in the range of 200-228 ohm^{-1} cm^{-1} mol^{-1} which confirmed that all the complexes are 1:2 electrolytes nature with free acetate ions.

UV-Vis and IR-Spectra:

The both Cu (II) complexes under the present study exhibits a broad band in the region 27210 cm^{-1}.and 26122 cm^{-1} were SB1-Cu and SB2-Cu respectively these were due to transition between $^2Eg \rightarrow {}^2Tg$. The both Ni (II) complex showed two bands between 25133-26113cm^{-1} and 27504-28123 cm^{-1} which is assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{2g}$ transition respectively. The spectral information from UV-VIS was well agreed with the octahedral geometry of the Cu^{2+} and Ni^{2+}complexes. The IR spectrum of the Schiff bases showed sharp band observed around 1655-1615cm^{-1} is assigned to the ν(C=N) mode of the azomethine group and this band shifts towards lower wave numbers around 1624-1601 cm^{-1} in all the complexes indicated that azomethine nitrogen involved in coordination. The aromatic ν(OH) group in the ligand SB1-L was observed around 3425-3375 cm^{-1} and the disappearance or reduced intensity of this band in the complexes confirmed that the –OH group was not free and involved in coordination. The presence of a new bands around 425-460 cm^{-1} and 536-570cm^{-1} in all the complexes assignable to ν(M-N) and ν(M-O) vibration frequency respectively. A sharp band observed at 1730 cm^{-1} in the SB2-L is assigned to amide ν(C=O) of isatin moiety and this band shifted towards lower wave numbers around 1724cm^{-1}in the corresponding metal complexes confirmed that amide group involved in coordination. The presence of coordinated water in all the complexes is confirmed by the presence of broad band around 3450 cm-1 and sharp band around 850 – 820cm^{-1}.due to stretching and bending vibration respectively.

^{1}H-NMR and ^{13}C-NMR spectra

The compound SB1-L showed two singlets at 15.07 and 13.14 δppm were due two aromatic OH group. The two singlet at 10.82 and 9.42 δppm were due to two CH=N proton and these are confirmation peak of schiff base formation. The remaining 16 aromatic protons appeared in between 7.18-8.36 δppm as several multiplets and methyl protons appeared at 2.48 δppm as singlet. The ^{13}C-NMR spectra of SB1-L showed following carbon signal 169.77,168.88 (2C-conneted with OH), 155.53,155.60 (2CH=N), 140.32, 139.25, 138.20, 137.68, 137.05, 136.74, 136.42, 135.40, 133.33, 132.98, 129.58, 129.40, 129.21, 128.09, 128.00, 127.89, 127.69, 127.50, 124.60, 123.56, 122.37, 122.09, 119.58, 119.37(24-aromatic carbon) and 21.33(CH_3) The compound SB2-L showed following protons signals at 2.31 δppm due aliphatic methyl protons and the weak, broad singlets at 3.97 and 1.62δppm due to 2NH proton. The remaining 11 aromatic protons appeared in between 6.6-7.83 as several multiplets. The SB2-L showed following ^{13}C-NMR signals at 170.27, 169.47(2C=N), 155.25(2C=O), 138.63, 136.98 (2C-connected with NH), 136.67, 136.53, 133.29, 133.22, 129.39, 128.11, 128.06, 127.42, 123.62, 123.57, 122.32, 122.08, 119.40, 119.08, 118.67, 109.32 (18- aromatic carbons) and 21.30 (CH_3)

Antibacterial activities

The antibacterial activities of both ligands (L) and their metal complexes were studied by usual agar disc diffusion method. The bacterial species used in the screening were staphylococcus aureus (gram positive) and Escherichia coli (gram negative). The presence of clear zones around the wells indicated that the compound is active. The diameter of the zone inhibition was deducted in millimeters by using zone diameter and the results showed that the chelating tends to make the ligands act as good anti-bactericidal agent thus killing more of the bacteria than the corresponding free ligands. The detailed antibacterial activity data given in **table- 2**

Table-2: Antibacterial activity of schiff bases and their metal complexes

No	Bacteria	Standard (streptomycin)	Zone of inhibition in mm (20µg/disc)					
			SB1 - L	SB1 - Cu	SB1 - Ni	SB2 - L	SB2 - Cu	SB2-Ni
1	*Staphylococcus aureus*	22	10	16	15	10	18	16
2	*Escherichia coli*	24	08	15	16	12	16	15

CONCLUSION

We synthesized two new schiff bases and their four transition metal complexes. The expected structures were confirmed with help of their physical and spectroscopic data. The SB2-L and its transition metal complexes showed good antibacterial activity than the SB1-L and its complexes against selective bacteria were observed.

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