

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF SOME NOVEL SCHIFF BASE COMPOUNDS OF TRANSITION METAL AND THEIR BIOLOGICAL STUDIES

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ABSTRACT

Cu (II) and Ni(II) complexes of novel Schiff base derived from 4, 5-Dimethoxy 1, 2-phenylenediamine and 5-substituted salicylaldehyde have been synthesized and characterized by means of various physico-chemical technique viz. elemental analysis, magnetic moment, IR, NMR and electronic spectral studies. The complexes have been found to have a stoichiometry of 1:1 (M:L), wherein azomethine nitrogen and phenolic oxygen of ligand is coordinated to metal. The probable geometry and biological activity of the complexes are also reported.

Keywords: novel schiff base, metal (II) complexes, biological activity.

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INTRODUCTION

During recent years, there has been considerable interest in the chemistry of transition metal complexes of Schiff base¹⁻³. This is due to the fact that Schiff base offer opportunities for substrate chirality, tuning the metal centred electronic factor, enhancing the solubility and stability of either homogeneous or heterogeneous catalysts⁴⁻⁹. It has also been observed that chelation causes drastic change in the biological properties of the ligand and the metal moiety. A large number of Schiff base complexes¹⁰⁻¹³ have been tested for antimicrobial activities and they have been found antibacterial, antifungal¹⁴⁻¹⁸, anticancer¹⁹⁻²⁰ and herbicidal²¹. The complexes containing O, N donor atoms are very important owing their significant antibacterial and anticancer activity²².

In the present paper we report the synthesis, spectroscopic characterization and biological activities of Cu (II) and Ni (II) complexes with Schiff base derived from 4, 5-Dimethoxy-1, 2-phenylenediamine and 5-substituted salicylaldehyde.

EXPERIMENTAL

Materials

All the chemicals and solvents used were of AR grade. The 4, 5-Dimethoxy-1, 2 –phenylenediamine and 5-substituted salicylaldehyde were obtained from Central Drug House, New Delhi.

Synthesis of Ligands

The Schiff base ligand was prepared by mixing an ethanolic solution of 4, 5-Dimethoxy-1,2-phenylenediamine with ethanolic solution of respective salicylaldehyde in a 1:2 stoichiometric ratio. The resulting solution then refluxed with stirring for 2 hr. The precipitate was collected by filtration, recrystallized from ethanol, and dried at room temperature (Fig.1).

Synthesis of Metal Complexes

A general method has been adopted for the isolation of complexes in solid state. Hot ethanolic solution of metal salt (CuCl₂.2H₂O and NiCl₂.5H₂O) and solution of respective ligand were mixed in 1:1 molar ratio. The resulting solution was refluxed with stirring for 2 hrs, and then kept overnight to insure the complete reaction. Thus, the formed complexes were filtered, collected and then washed with hot ethanol until the filtrate becomes colourless. The complexes were dried in desiccators (Fig.2).

Measurements

Elemental analysis (CHN) was performed on Elemental Vario EL-III automatic equipment. The IR spectra were recorded on Thermo-Nicolet Nixus FTIR automatic recording spectrophotometer. Shimadzu UV and visible spectrophotometer 1601 CP provided with an automatic recorder was used to record the electronic spectra. The magnetic susceptibility of all the metal complexes was determined using Gouy's method, suspending the specimen tube filled with the powdered complex. Mercury (II) tetra thiocyanate cobaltate (II) $\text{HgCo}(\text{CNS})_4$ was used as calibrant.

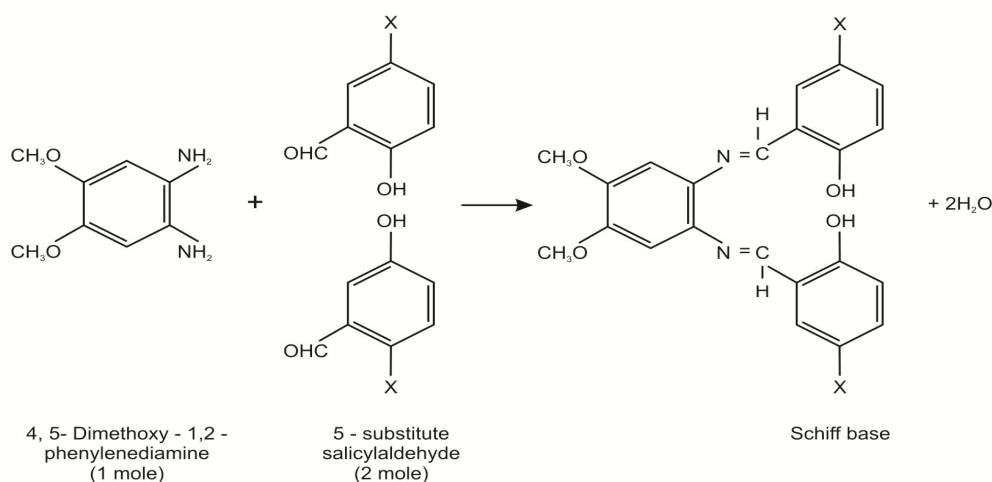


Fig.1. Structure of Schiff base (ligand)

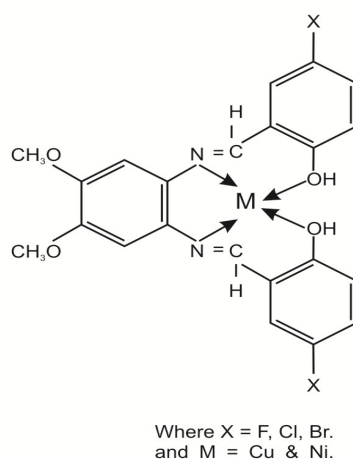


Fig.2. Structure Proposed (Metal Complex)

RESULTS AND DISCUSSION

Elemental Analysis

The compositional data of the synthesized compounds are in good agreement with their suggested stoichiometries Table-1. All the metal complexes are soluble in common organic solvents such as DMF and DMSO.

Table-1: Analytical Data of Schiff base and Metal Complexes

S.No.	Molecular Formula	Molecular Weight	Yield %	Elemental Analysis (%)				
				Calculated (Observed)				
				C	H	N	X	M
1	C ₂₂ H ₁₈ N ₂ O ₄ Cl ₂ (L ₁)	445	76	59.32 (59.21)	4.04 (4.06)	6.30 (6.42)	15.95 -	- -
2	C ₂₂ H ₁₈ N ₂ O ₄ Cl ₂ Cu(Cu-L ₁)	508.5	88	51.92 (51.79)	3.54 (3.50)	5.51 (5.57)	13.96 (13.82)	12.48 -
3	C ₂₂ H ₁₈ N ₂ O ₄ Cl ₂ Ni(Ni-L ₁)	503.7	84	52.41 (52.48)	3.57 (3.81)	5.56 (5.48)	14.10 -	11.65 -
4	C ₂₂ H ₁₈ N ₂ O ₄ Br ₂ (L ₂)	534	71	49.44 (49.50)	3.37 (3.32)	5.24 (5.21)	29.96 -	- -
5	C ₂₂ H ₁₈ N ₂ O ₄ Br ₂ Cu(Cu-L ₂)	597.5	82	44.18 (44.12)	3.01 (3.07)	4.68 (4.61)	26.78 -	10.63 -
6	C ₂₂ H ₁₈ N ₂ O ₄ Br ₂ Ni(Ni-L ₂)	602.7	84	43.80 (43.78)	2.98 (2.93)	4.65 (4.70)	26.55 -	9.74 -
7	C ₂₂ H ₁₈ N ₂ O ₄ F ₂ (L ₃)	412	68	64.08 (64.11)	4.37 (4.37)	6.80 (6.72)	9.22 -	- -
8	C ₂₂ H ₁₈ N ₂ O ₄ F ₂ Cu(Cu-L ₃)	475.5	72	55.5 (55.42)	3.78 (3.81)	5.89 (5.92)	7.99 -	13.35 -
9	C ₂₂ H ₁₈ N ₂ O ₄ F ₂ Ni(Ni-L ₃)	470.7	84	56.08 (56.14)	3.82 (3.87)	5.92 (5.81)	8.07 -	12.47 -

Infrared Spectra

The IR data are presented in the Table-2. Comparison of the IR spectra of the Schiff base ligands with that of its complexes show the absorption bands in the range 1612-1630 cm⁻¹ and 1366-1380 cm⁻¹ due to azomethine $\nu(\text{C}=\text{N})$ and phenolic $\nu(\text{C}-\text{O})$ groups respectively. The $\nu(\text{C}=\text{N})$ vibrations decreased by 24-30 cm⁻¹ on complexation showing involvement of nitrogen of azomethine group in coordination²³. The absence of stretching and bending vibrations of free carbonyl group at ~1700 cm⁻¹ indicates the absence of this group in these complexes²⁴. Further the phenolic (C-O) vibrations on complexation with Cu(II) and Ni(II) ions has also shown a shift to higher frequency indicating the coordination of both the ions through phenolic oxygen of the schiff base and azomethine nitrogen. The band in the range 3326 - 3338 cm⁻¹ due to phenolic- OH in the ligands is shifted to higher frequency in all the complexes indicating the coordination of phenolic oxygen to the metal ion without deprotonation²⁵. The (C-O) stretching frequency is generally displaced to higher frequency indicating the formation of bond between the oxygen of phenolic group and metal²⁶⁻²⁷.

For the free ligands the broad band in the range 2937-3174 cm⁻¹ are assigned to the -OH group vibration associated intramolecularly with the nitrogen atom of the CH=N group²⁸. These bands disappear on complexation with metal ions, which is an evidence for coordination of Cu (II) and Ni (II) ions through phenolic oxygen.

Presence of new bands in the region 466-482 cm⁻¹ and 517-546 cm⁻¹ due to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ respectively also support the coordination of ligand through azomethine nitrogen and phenolic oxygen atom with metal²⁹.

Table-2: Selected IR frequencies of Schiff base and its metal complexes (cm⁻¹)

S.No.	Compound	$\nu(\text{C}-\text{H})$	$\nu(-\text{OH})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}-\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
1	L	3055	3332	1366	1622	-	-
2	Cu-L ₁	3048	3346	1378	1598	468	522
3	Ni-L ₁	3070	3332	1381	1592	471	518
4	L ₂	3221	3326	1380	1612	-	-
5	Cu-L ₂	3230	3342	1392	1582	466	538

6	Ni-L ₂	3218	3350	1397	1596	472	517
7	L ₃	3140	3338	1375	1630	-	-
8	Cu-L ₃	3157	3352	1393	1605	476	540
9	Ni-L ₃	3181	3356	1387	1608	482	546

UV-visible electronic spectra and magnetic susceptibility measurements

The electronic spectral data of the ligands and its complexes are presented in the Table-4. These data also support the structural formation of the ligand and complexes. The band observed in the range 252-270 nm is attributed to benzene $\pi \rightarrow \pi^*$ transitions. The band in the range 326-338 nm assignable to $n \rightarrow \pi^*$ transition of non-bonding electrons present on the nitrogen of the azomethine group in the ligand. After complexation this azomethine group of ligand changes to azomethine linkage in all the copper and nickel complexes which is confirmed through the presence of intense band around 345-352nm, and 342-356nm respectively and assigned to $n \rightarrow \pi^*$. The Cu(II) complexes showed absorption band in the range 428-436 nm, which is assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition, a characteristic of square planer geometry³⁰.

On the other hand Ni(II) complexes showed bands in the range 492-504 nm, which is assigned to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition, also a characteristic of square planner geometry³⁰.

Table-3: Magnetic Moment of Metal Complexes

S.No.	Complex	Magnetic moment (BM)
1	Cu-L ₁	1.91
2	Ni-L ₁	2.96
3	Cu-L ₂	1.72
4	Ni-L ₂	3.12
5	Cu-L ₃	2.06
6	Ni-L ₃	3.08

Table-4: Electronic Spectral and NMR data of the schiff base ligand and its complexes

S.No.	Compound	λ_{\max} (nm)	${}^1\text{H}$ NMR data (as ppm)				${}^{13}\text{C}$ NMR data (as ppm)	
			-OH	Ar	HC=N	-OCH ₃	HC=N	-OCH ₃
1	L ₁	252, 335	13.81	6.82-7.56	8.89	3.76	164.2	57.2
2	Cu-L ₁	277, 352, 436		6.53-7.21	9.01	3.78	165.4	57.9
3	Ni-L ₁	274, 342, 498		6.72-7.39	9.10	3.81	166.2	58.1
4	L ₂	270, 326	13.23	6.94-7.62	8.98	3.72	168.9	55.2
5	Cu-L ₂	278, 345, 428		6.59-7.38	9.12	3.80	173.4	56.4
6	Ni-L ₂	280, 356, 492		6.73-7.49	9.20	3.86	171.2	58.7
7	L ₃	268, 338	12.94	7.10-7.72	8.97	3.85	162.6	55.8
8	Cu-L ₃	277, 350, 431		6.98-7.62	9.16	3.88	170.4	57.2
9	Ni-L ₃	280, 353, 504		6.94-7.61	9.17	3.79	168.2	58.1

The Cu (II) complexes show magnetic moment in the range 1.72-2.06 BM corresponding to the presence of one unpair electron, hence attributed to low spin square planer structure for Cu (II) complexes³¹. Similarly Ni (II) complexes show magnetic moment in the range 2.92-3.12 BM corresponding to the presence of two unpaired electron, it also support the structure proposed Table-3.

${}^1\text{H}$ NMR and ${}^{13}\text{C}$ NMR spectra

Further evidence for the coordination of the ligand to the metal ions Cu (II) and Ni(II) is provided by the ${}^1\text{H}$ NMR and ${}^{13}\text{C}$ NMR. All these spectra are given in the Table-4. The ${}^1\text{H}$ NMR spectra of the Schiff base exhibits a singlet signal in the region δ 8.89-8.98 and multiplet in the region δ 6.82-7.72 attributed to azomethine protons³² and aromatic protons³³ respectively. The ${}^1\text{H}$ NMR spectra of Schiff base ligand showed slight signal in the region δ 12.94-13.81 attributed to two phenolic -OH protons. In addition, the

signals of azomethine protons of metal complexes shifted to downfield region δ 9.01-9.20 in comparison with that of the free ligands. This confirm the involvement of N-atom with metal ions³⁴. The ^1H NMR spectra of Schiff base also exhibits a multiplet at δ 3.72-3.85 attributed to $-\text{OCH}_3$ protons, it was also observed in the metal complexes.

In the ^{13}C NMR spectra, the signals at δ 55.2-58.7 is attributed to $-\text{OCH}_3$ carbon³⁵ and the signals at δ 162.6-173.4 is attributed to azomethine carbon.

Table-5: Antimicrobial effects of the ligands and their metal complexes

S.No.	Compound	Inhibition Zone (mm)				
		E.Coli	S.epidermidis	A.flavus	A.niger	C.lunata
1	L_1	7	6	9	11	10
2	Cu-L_1	12	16	15	14	18
3	Ni-L_1	14	15	14	16	15
4	L_2	9	8	13	10	11
5	Cu-L_2	15	14	16	16	17
6	Ni-L_2	14	16	17	13	18
7	L_3	8	7	12	12	10
8	Cu-L_3	12	11	14	15	16
9	Ni-L_3	14	15	15	14	18

Antimicrobial Studies

The antimicrobial activities of ligands and its complexes were tested in vitro against *S. epidermidis*, *E. Coli*, *A. flavus*, *A. niger* and *C. lunata* by reported method³⁶. On comparing the antimicrobial activities of schiff base ligand and its metal (Cu, Ni) complexes, we found that the complexes exhibit more activity then that of the ligands. The increase in the activity of the complexes compared to that of the ligands could be explained on the basis of Overtone's concept³⁷ and Tweedy's chelation theory³⁸ table (5). It has also been found that the ligands showed no activity against *E.coli*.

CONCLUSIONS

On the basis of above mentioned studies we can proposed the square planer geometry for the metal complexes and the antimicrobial results showed that these metal complexes were more potent then that of Schiff base ligands.

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[RJC-1018/2013]