Synthesis and Spectroscopic Characterization of Some Novel Schiff Base Complexes of Transition Metals and Their Biological Studies

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Cobalt(II) and manganese(II) complexes of novel Schiff base derived from 4,5-dimethoxy-1,2-phenylenediamine and 5-substituted salicylaldehyde have been synthesized and characterized by various physico-chemical techniques *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). The probable geometry and biological activity of the complexes also have been reported.

Keywords: Novel Schiff base, Co(II), Mn(II) Complexes, Biological activity.

INTRODUCTION

The condensation of primary amine with carbonyl compounds yields Schiff base¹⁻³. The resultant imines ($R_1HC=N-R_2$) participate in binding with metal ions *via* nitrogen lone pair electrons. In the recent years, there has been considerable interest in the chemistry of transition metal complexes of Schiff base⁴⁻⁶. 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 catalysts⁷⁻¹². Schiff base-transition metal complexes are one of the most adaptable and thoroughly studied systems¹³⁻¹⁴. These complexes have also applications in clinical¹⁵ and analytical fields¹⁶. Some of Schiff base complexes are used as model molecules for biological oxygen carrier systems¹⁷. A large number of Schiff base complexes¹⁸⁻²¹ have been tested for antimicrobial activities and they have been found antibacterial, antifungal²²⁻²⁶, anticancer^{27,28} and herbicidal²⁹. Tetradentate Schiff base complexes are well known to form stable complexes, where the coordination takes place through the N_2O_2 donor set³⁰⁻³².

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

EXPERIMENTAL

All the chemicals and solvents used were of AR grade. 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 of ethanolic solution of 4,5-dimethoxy-1,2-phenylenediamine (1 mol) with an ethanolic solution of respective salicylaldehyde (2 mol) in a 1:2 stoichiometric ratio. The resulting solution then refluxed with stirring for 2 h. The precipitate was collected by filtration, recrystallized from ethanol and dried at room temperature (**Scheme-I**).

Scheme-I: Synthesis of ligand (where X = F, Cl, Br)

Synthesis of metal complexes: A general method has been adopted for the isolation of complexes in solid state. Hot ethanolic solution of metal salts ($CoCl_2 \cdot 6H_2O$ and $MnCl_2 \cdot 4H_2O$) and solution of respective ligand were mixed in 1:1 molar ratio. The resulting solution was refluxed with stirring for 4 h 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 a desiccators (Fig. 1).

Fig. 1. Proposed structure of metal complex

Elemental analysis 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) tetrathiocyanate cobaltate(II) $\text{HgCo}(\text{CNS})_4$ was used as calibrant.

RESULTS AND DISCUSSION

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.	Mol. Formula	m.w.	Yield (%)	Elemental calculated (Observed)			
				C	H	N	M
1	$\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_4\text{Cl}_2(\text{L}_1)$	445	76	59.32 (59.21)	4.04 (4.06)	6.30 (6.42)	-
2	$\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_4\text{Cl}_4\text{Co}(\text{CoL}_1)$	573	82	46.07 (46.12)	2.80 (2.82)	4.89 (4.87)	10.30 (10.28)
3	$\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_4\text{Cl}_4\text{Mn}(\text{MnL}_1)$	569	87	46.40 (46.32)	2.81 (2.72)	4.92 (4.91)	9.67 (9.61)
4	$\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_4\text{Br}_2(\text{L}_2)$	534	71	49.44 (49.50)	3.37 (3.32)	5.24 (5.21)	-
5	$\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_4\text{Br}_2\text{Co}(\text{CoL}_2)$	662	79	39.88 (39.80)	2.42 (2.49)	4.23 (4.28)	8.91 (8.87)
6	$\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_4\text{Br}_2\text{Cl}_2\text{Mn}(\text{MnL}_2)$	658	83	40.12 (40.08)	2.43 (2.40)	4.35 (4.21)	8.36 (8.40)
7	$\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_4\text{F}_2(\text{L}_3)$	412	68	64.08 (64.11)	4.37 (4.37)	6.80 (6.72)	-
8	$\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_4\text{F}_2\text{Cl}_2\text{Co}(\text{CoL}_3)$	540	84	48.89 (48.81)	2.36 (2.96)	5.18 (5.21)	10.92 (10.93)
9	$\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_4\text{F}_2\text{Cl}_2\text{Mn}(\text{MnL}_3)$	536	77	49.25 (49.26)	2.98 (2.91)	5.22 (5.18)	10.21 (10.26)

Infrared spectra: The IR data of the Schiff base and its complexes are listed in Table-2. Comparison of the IR spectra

TABLE-2
SELECTED IR FREQUENCIES OF SCHIFF BASE
AND ITS METAL COMPLEXES (cm^{-1})

S. No.	Com.	$\nu(\text{-H})$	$\nu(\text{-OH})$	$\nu(\text{C-O})$	$\nu(\text{C-N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-Co})$
1	L_1	3055	3332	1366	1622	-	-	-
2	Co-L_1	3042	3342	1350	1596	432	532	312
3	Mn-L_1	3062	3340	1341	1604	448	517	317
4	L_2	3221	3326	1380	1612	-	-	-
5	Co-L_2	3228	3346	1367	1591	420	541	305
6	Mn-L_2	3232	3348	1365	1597	438	546	308
7	L_3	3140	3338	1375	1680	-	-	-
8	Co-L_3	3148	3355	1365	1668	463	522	306
9	Mn-L_3	3170	3351	1352	1655	450	537	314

of Schiff base ligands with that of its complexes show the absorption bands in the range $1630\text{-}1612\text{ cm}^{-1}$ and $1380\text{-}1366\text{ cm}^{-1}$ due to azomethine $\nu(\text{C=N})$ and phenolic $\nu(\text{C=O})$ groups respectively. The (C=N) vibrations decreased by $12\text{-}26\text{ cm}^{-1}$, on complexation showing involvement of nitrogen of azomethine group in coordination³³. This is further substantiated by the presence of a new band around $463\text{-}420\text{ cm}^{-1}$ assignable to $\nu(\text{M-N})$ ³⁴. The absence of stretching and bending vibrations of free carbonyl group at about 1700 cm^{-1} indicates the absence of this group in these complexes³⁵. The (C-O) vibrations decreased by $10\text{-}25\text{ cm}^{-1}$ relative to the free ligands suggesting involvement of the oxygen atom of the C-O moiety in coordination³⁶. Presence of new bands in the region $546\text{-}517\text{ cm}^{-1}$ due to $\nu(\text{M-O})$ also support the coordination of ligand through phenolic oxygen with metal³⁷.

Thus, it can be concluded that the Schiff base is a tetradentate ligand coordinating *via* the azomethine N and the phenolic O. The infrared spectra show bands in the region $317\text{-}305\text{ cm}^{-1}$ corresponding to (M-Cl) vibrations³⁸.

Electronic spectra: The electronic spectra of the ligand and complexes are summarised in Table-5. These data also support the structural formulae of the ligand and complexes. The band observed in the range $252\text{-}270\text{ nm}$ is attributed to benzene $\pi \rightarrow \pi^*$ transitions. The band in the range $326\text{-}338\text{ nm}$ assignable to $\pi \rightarrow \pi^*$ transitions of non-bonding electrons present in the nitrogen of the azomethine group on the ligand. After complexation this azomethine group of ligand changes to azomethine linkage in all the cobalt and manganese complexes which is confirmed through the presence of intense band around $345\text{-}352$ and $342\text{-}356\text{ nm}$, respectively and assignable to $\pi \rightarrow \pi^*$.

TABLE-3
ANTIMICROBIAL EFFECTS OF THE LIGANDS
AND THEIR METAL COMPLEXES

S. No.	Com.	Inhibition zone (mm)				
		<i>E. Coli</i>	<i>S. epidermidis</i>	<i>A. flavus</i>	<i>A. Niger</i>	<i>C. Lunata</i>
1	L_1	7	6	9	11	10
2	Co-L_1	13	15	15	12	11
3	Mn-L_1	12	16	14	15	18
4	L_2	9	8	13	10	11
5	Co-L_2	15	16	14	16	12
6	Mn-L_2	14	15	17	13	14
7	L_3	8	7	12	12	10
8	Co-L_3	12	14	16	17	17
9	Mn-L_3	13	11	15	14	16

Cobalt(II) complexes showed absorption band in the range 467-481 and 312-348 nm. The bands can be assigned to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow 4T_{1g}(P)$ transitions, respectively which are in accordance with Co(II) high spin octahedral geometry³⁹. Further the magnetic moment of Co(II) complexes (4.58-4.89) BM suggest a high spin octahedral geometry⁴⁰ (Table-4).

TABLE-4
MAGNETIC MOMENT OF METAL COMPLEXES

S. No.	Complex	Magnetic moment (BM)
1	Co-L ₁	4.67
2	Mn-L ₁	5.83
3	Co-L ₂	4.58
4	Mn-L ₂	5.94
5	Co-L ₃	4.89
6	Mn-L ₃	5.97

Manganese(II) complexes showed bands in the range 618-625, 490-503, 478-484, 375-390 nm which are assigned to ${}^6A_{1g} \rightarrow {}^6T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$, ${}^6A_{1g} \rightarrow {}^4E_g$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}$, respectively, a characteristic of octahedral geometry⁴¹. The magnetic moment of Mn(II) complexes lie in the range 5.83-5.97 BM, which is indicative of octahedral geometry⁴².

¹H NMR and ¹³C NMR spectra: Further evidence for the coordination of the ligand to the metal ion Co(II) and Mn(II) is provided by the ¹H NMR and ¹³C NMR. All these spectra are given in the Table-5. The ¹H 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 protons⁴³ and aromatic protons⁴⁴, respectively. The ¹H 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 9.07- δ 9.31 in comparison with that of the free ligands. This confirm the involvement of N-atom with metal ions⁴⁵. The ¹H NMR spectra of Schiff base also exhibits a multiplet at δ 3.72-3.85 attributed to -OCH₃ protons, it was observed in the metal complexes.

TABLE-5
ELECTRONIC SPECTRAL AND NMR DATA OF
SCHIFF BASE LIGAND AND ITS COMPLEXES

S. No.	Comp.	λ_{max} (nm)	¹ H NMR data (at ppm)				¹³ C NMR data (at 10 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	Co-L ₁	477, 312		6.76-6.93	9.06	3.77	164.3	57.4
3	Mn-L ₁	625, 493		6.51-7.22	9.07	3.81	165.5	57.5
4	L ₂	270, 326	13.23	6.94-7.62	8.98	3.72	168.9	55.2
5	Co-L ₂	467, 348		6.68-7.41	9.06	3.76	170.1	55.8
6	Mn-L ₂	621, 490		6.75-7.11	9.13	3.78	171.4	56.2
7	L ₃	268, 338	12.94	7.10-7.72	8.97	3.85	162.6	55.8
8	Co-L ₃	481, 337		6.83-7.34	9.18	3.86	168.3	56.9
9	Mn-L ₃	503, 618		6.92-7.40	9.12	3.81	170.2	57.2

In ¹³C NMR spectra, the signals at δ 55.2-58.7 is attributed to -OCH₃ carbon⁴⁶ and the signals at δ 162.6-173.4 is attributed to azomethine carbon.

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 method⁴⁷. On comparing the antimicrobial activities of Schiff base ligand and its metal 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 concept⁴⁸ and Tweedy's chelation theory⁴⁹.

Conclusion

On the basis of above mentioned studies, we have proposed the octahedral geometry for the metal complexes and the antimicrobial results showed that these metal complexes are more potent then that of Schiff base ligands.

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