

Synthesis and Spectroscopic Characterization of some novel Schiff base Complexes of Ru(III) and their biological screening

Netra Pal Singh*, Poonam Saini, Asvini Kumar, Krishan Kumar

Abstract: Ru(III) 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, TGA and electronic spectral studies. The complexes have found a stoichiometry of 1:1 (M:L), where in azomethine nitrogen and phenolic oxygen of ligand is coordinated to ruthenium. These studies revealed an octahedral geometry for all the complexes. The ligands and their complexes were screened for their antimicrobial studies.

Keywords: novel Schiff base, Ru(III) complexes, antimicrobial studies.

1 Introduction

During recent years, there has been considerable interest in the chemistry of transition metal complexes of Schiff base [1,2]. Due to their increasing potential as versatile catalysts for organic synthesis and polymer chemistry, ruthenium complexes witnessed a spectacular development during the last decade. Several families of ruthenium complexes have been prepared and extensively used in a variety of chemical transformation such as hydrogenation, hydration[3], oxidation[4], epoxidation [5], isomerization[6], decarbonylation [7], cyclopropanation[8], olefin metathesis[9], Diels-Alder reaction[10], enol-ester synthesis[11].

In the present paper we report the synthesis and characterization of novel Schiff base complexes of ruthenium (III) and their biological activity.

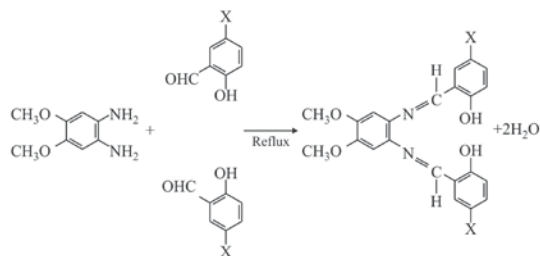
2 Experimental

2.1 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.

2.2 Synthesis of Ligands

The Schiff base ligand were 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 (Scheme 1).



4, 5-dimethoxy-1, 2- phenylenediamine + 5-substituted salicylaldehyde → Schiff base (where X=Cl, Br, F) + 2H₂O

(1 mole)

(2 mole)

Scheme 1. Structure of Schiff Base

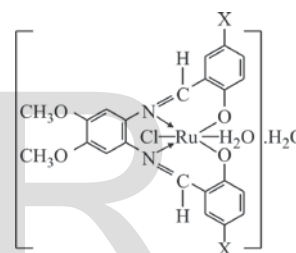


Fig.1. Structure of Ruthenium Complex.

2.3 Synthesis of Ruthenium Complexes

A general method has been adopted for the isolation of complexes in solid state. Hot ethanolic solution of RuCl₃.3H₂O and solution of respective ligand were mixed in 1:1 molar ratio. The resulting solution was refluxed with stirring for 4-5 hrs, and then kept overnight to insure the complete reaction. The formed complexes were filtered, collected and then washed with hot ethanol until the filtrate becomes colourless. The complexes were dried in a desiccators(Fig1).

4 Physical measurements

Elemental analysis (C, H, N) were performed using a VarioEL elemental analysensysteme. Metals and chlorides were determined volumetrically [12] and gravimetrically [13] respectively. IR spectra were recorded using KBr discs (4000-400 cm⁻¹) on a Shimadzu 8300 IR spectrophotometer. Electronic absorption spectra in the 200-900 nm range were obtained in DMF on a Systronic UV-visible spectrophotometer. ¹H NMR and ¹³C NMR spectra (at room temperature) (in DMSO-d₆) were recorded on a Bruker Avance II 400 NMR spectrometer with reference to TMS (tetramethylsilane) (0.0 ppm). Molar conductance measurements were determined in DMSO (~10⁻³ M) at room temperature using a Jenway Model 4070 conductivity meter. Magnetic moment measurement were carried out by the Gouy method using Hg[Co(SCN)₄] as calibrant.

5 Results and Discussion

5.1 Elemental Analysis

The compositional data of the ruthenium (III) complexes are in good agreement with their suggested stoichiometries. All these complexes are soluble in common organic solvents such as DMF and DMSO (Table 1).

Table 1: Analytical Data of Schiff base and metal complexes

S.No	Molecular formula	Mol wt.	Yield %	Elemental Analysis (%) calculated (Observed)			
				C	H	N	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)	-
2.	C ₂₂ H ₂₂ N ₂ O ₆ Cl ₃ Ru	617.57	82	42.75 (42.68)	3.56 (3.51)	4.53 (4.53)	17.24
3.	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)	-
4.	C ₂₂ H ₂₂ N ₂ O ₆ Br ₂ Ru	706.57	78	37.36 (37.30)	3.11 (3.02)	3.96 (3.87)	14.30
5.	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)	-
6.	C ₂₂ H ₂₂ N ₂ O ₆ F ₂ Ru	584.57	83	45.16 (45.14)	3.76 (3.72)	4.79 (4.75)	17.29

5.2 Infrared Spectra

The preliminary identification regarding the formation of the free Schiff base and its complexes were obtained from IR spectral data (Table 2). The Schiff base ligand shows a strong band in the range 1612-1630 cm⁻¹ due to azomethine ν (C=N) and another bands in the range 1366–1380 cm⁻¹ due to phenolic ν (C-O) group. On complexation the (C=N) vibrations decreased by 12-27 cm⁻¹ showing involvement of nitrogen of azomethine group in coordination[14]. This is further substantiated by the presence of a new band around 466-507 cm⁻¹ assignable to ν (M-N) [15]. The absence of stretching and bending vibrations of free carbonyl group at around 1700 cm⁻¹ indicates the absence of this group in these complexes. [16] This may be due to the enolisation and subsequent coordination through the deprotonated enolised oxygen atom[17,18]. Another medium intensity band around 3300 cm⁻¹ in the free ligands due to phenolic ν (OH) [19] was absent in the complexes also support the deprotonation of the Schiff base prior to the coordination. This is further supported by the increase in the phenolic ν (C-O) vibration by 14-27 cm⁻¹ [20,21] Presence of new band in the region 521-538 due to (Ru-O) also support the coordination of ligand through phenolic oxygen with ruthenium[22]. The infrared spectra show bands in the region 306-319 cm⁻¹ corresponding to (Ru-Cl) vibrations[23]. Two additional new bands are observed in the range 1641-1662 cm⁻¹ and

847-856 cm⁻¹ due to the bending and rocking motions of H₂O[24]. The latter band is characteristic for coordinated H₂O molecule and is further confirmed by TGA/DTA Analysis.

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

S.No.	Compound	ν (CH)	ν (OH)	ν (CO)	ν (CN)	ν (M-N)	ν (M-Cl)	ν (M-O)
1.	L ₁	3055	3332	1366	1622	-	-	-
2.	Ru-L ₁	3062	-	1381	1585	471	319	530
3.	L ₂	3221	3326	1380	1612	-	-	-
4.	Ru-L ₂	3233	-	1394	1600	466	306	538
5.	L ₃	3140	3338	1375	1630	-	-	-
6.	Ru-L ₃	3129	-	1402	1612	507	310	521

5.3 Electronic Spectra

The electronic spectra of the ligands and complexes are summarized in Table 3. These data also support the structural formation of the ligands and complexes. The electronic spectra of the ground state of Ru(III) is ²T_{2g} and the first excited doublet levels in the order of increasing energy are ²A_{2g} and ²A_{1g} which arise from the t_{2g}⁴e_g¹ configuration. [25] In most of the Ru(III) complexes, the UV-vis spectra show only charge transfer bands[26].

The electronic spectral data for ligands show mainly two absorption bands in the region 252-270 nm and 326-338 nm. 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 $\rightarrow \pi^*$ transitions of non-bonding electrons present in the nitrogen of the azomethine group on the ligands. After complexation the azomethine group of ligands change to azomethine linkage in all the Ru(III) complexes(Fig.2).

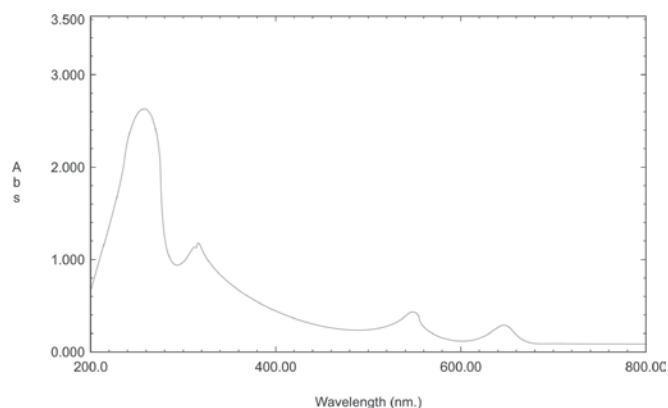


Fig 2. UV-visible spectra of Ruthenium complex

The electronic spectra of Ru (III) complexes exhibit mainly three bands in the range 352-361 nm, 536-551 nm, and 620-647 nm respectively. The band in the range 352-361nm are considered as d-d transition ²T_{1g} \rightarrow ²A_{2g} and the band in the range 536-551nm may be assigned to M-L _{π} * transitions ²T_{2g} \rightarrow ²E_g. The band in the range 620-647 nm are assignable to interligand transition or to

MLCT band ${}^2T_{2g} \rightarrow {}^2A_{1g}$. Similar observations have been made for other Ru (III) octahedral complexes[27]. Further the In the present paper we report the synthesis and characterization of novel Schiff base complexes of ruthenium (III) and their biological activity.

5.4 1H NMR and ${}^{13}C$ NMR Spectra

These spectra are summarized in the Table 4. The 1H NMR spectra of 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 protons[29] and aromatic protons[30] 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. The 1H NMR spectra of Schiff-base also exhibits a multiplet at δ 3.72-3.85 attributed to -OCH₃ protons.

In the ${}^{13}C$ NMR spectra, the signals at δ 55.2-58.7 is attributed to -OCH₃ carbon[31] and the signals at δ 162.6-173.4 is attributed to azomethine carbon.

Table3: Electronic spectral data of Schiff base and their ruthenium complexes

S.No.	Compound	λ_{max} (nm)
1.	L ₁	252,335
2.	Ru-L ₁	255, 359, 352,550,647
3.	L ₂	270,326
4.	Ru-L ₂	268, 361, 361,551,623
5.	L ₃	268,338
6.	Ru-L ₃	263, 352, 357,536,620

Table-4: 1H and ${}^{13}C$ NMR data of Schiff bases and their ruthenium complexes

S.No.	Compound	1H NMR data (as ppm)				${}^{13}C$ NMR data (as ppm)	
		-OH	Ar	HC=N	-OCH ₃	HC=N	-OCH ₃
1.	L ₁	13.81	6.82-7.56	8.89	3.76	164.2	57.2
2.	L ₂	13.23	6.94-7.62	8.98	3.72	168.9	55.2
3.	L ₃	12.94	7.10-7.72	8.97	3.85	162.6	55.8

Table-5: Magnetic Moment of ruthenium complexes

S.No.	Complex	Magnetic moment (BM)
1.	Ru-L ₁	1.92
2.	Ru-L ₂	1.88
3.	Ru-L ₃	1.87

5.5 Antimicrobial Studies

The in vitro antimicrobial screening of the free ligands, and its ruthenium (III) complexes were tested against *E.coli*, *Salmonella typhi*, *Staphylococcus aureus*, *Aspergillus niger* and *Curvularia lunata* by reported method [32]. On comparing the antimicrobial activities of Schiff base and its Ru (III) complexes, we found that the complexes exhibit more activity than that of the ligands(Fig3). The increase in the activity of the complexes compared to that of the ligands could be explained on the basis of overton's concept[33] and Tweedy's chelation theory[34]. It was interesting to note that the prepared complexes exhibited biological activity comparable to the well-known antibiotics and antifungals such as streptomycin and chlorometazole.

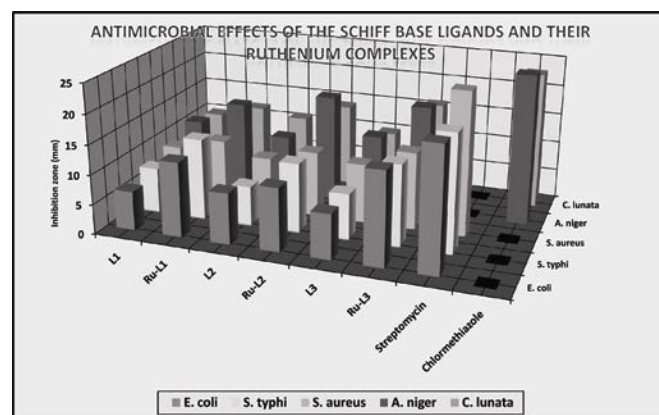


Fig 3. Antimicrobial activity bar graph

Table-6: Antimicrobial effects of the Schiff base and their ruthenium complexes

S.No.	Compound	Inhibition zone (mm)				
		E. coli	S. typhi	S. aureus	A. niger	C. lunata
1.	L ₁	7	8	9	11	10
2.	Ru-L ₁	13	14	11	15	12
3.	L ₂	9	7	9	10	11
4.	Ru-L ₂	11	12	11	18	14
5.	L ₃	8	8	10	12	10
6.	Ru-L ₃	16	14	13	18	16
7.	Streptomycin	21	20	24	-	-
8.	Chloromatazole	-	-	-	25	23

6 Conclusion

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

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Department of Chemistry, Meerut College, Meerut- 250001 U.P. (India)
*E-mail: npsmcm.in@gmail.com

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