

Synthesis and Characterization of Complex Compounds of Ruthenium (III) with 2-aminophenol and 2-nitroaniline Schiff base Ligands derived from 2-hydroxyl-1-naphthaldehyde

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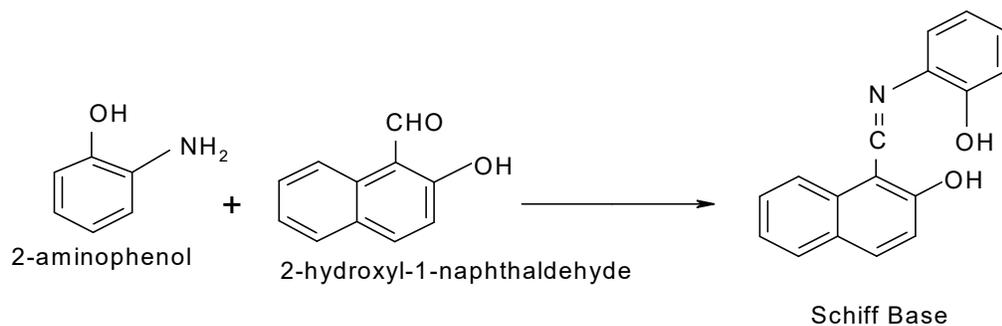
Abstract: The complexes of Ru(III) derived from 2-hydroxyl-1-naphthaldehyde ligands, (HL1 and HL2), were synthesized and characterized using ¹H NMR, ¹³C{H}NMR, FT-IR, UV-Vis, elemental (CHN)/metal content analysis and Conductivity measurement. The IR spectral data showed that the ligands acted as indented ligands coordinated to the Ru(III) ion through phenolic oxygen atom of the hydroxyl group (O-H), and the nitrogen atom of the azomethine (HC=N), whereas the bond that occurred via oxygen atom of the water molecule completed the geometry.

Keywords: 2-nitroaniline, 2-aminophenol, Metal complexes, 2-hydroxyl-1-naphthaldehyde, Schiff bases.

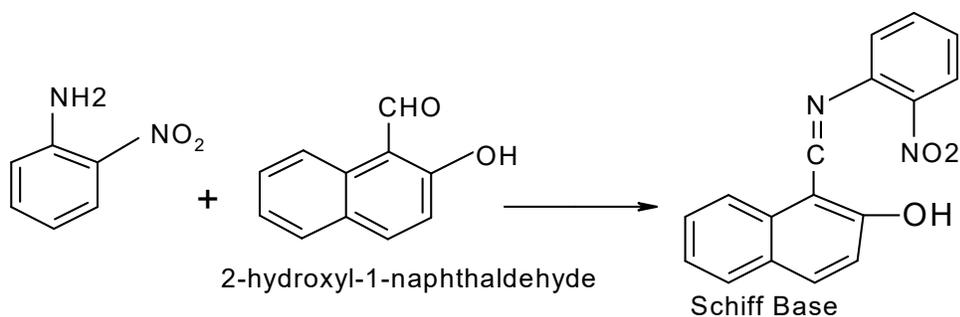
INTRODUCTION

Schiff bases have gained recognition as one of the frontline ligands in the field of coordination chemistry due to their stability, flexibility toward coordination, ease of synthesis and structural diversity. These ligands are good chelating agents toward transition and main group metals (Abbas, and Refat, *et al.*, 2016).

In recent time, Schiff bases derived from amines with aldehydes or ketones (from 2-hydroxyl-1-naphthaldehyde) are gaining more attention due to their versatility (Ayyavoo *et al.*, 2021 and (Fugu, *et al.*, 2013). Schiff base of 2-nitroaniline and 2-amino phenol (Figure 1), are class of compounds containing RC=NH group and they are obtained via condensation of amines with aldehydes or ketones (Lv, *et al.* and Naureen, *et al.*, 2021).



Scheme 1: Schiff base derived from 2-aminophenol and 2-hydroxyl-naphthaldehyde



Scheme 2: Schiff base derived from 2-nitroaniline and 2-hydroxyl-naphthaldehyde

Schemes shows the Schiff base derived from (a) 2-aminophenol and 2-hydroxyl-1-naphthaldehyde and (b). 2-nitroaniline with 2-hydroxyl-1-naphthaldehyde and this gave them ability to coordinate to metals in 1:1. The chemistry of these compounds, especially those containing oxygen and nitrogen donor atom together with their metal complexes are receiving attention owing to their fascinating biological activities (Daravath, *et al.*, and Savcı, *et al.*, 2021). Chemotherapeutic ability of Ruthenium complexes and its derivatives in the management of various diseases is well known (Bonnett, *et al.*, 2018 and de Faria, *et al.*, 2021). The Schiff base ligands reported here in these research work were synthesized via condensation of 2-aminophenol and 2-nitroaniline with 2-hydroxyl-1-naphthaldehyde in methanol as solvent at room temperature.

MATERIALS AND METHODS

All chemicals and solvents were reagent grade and used as received. These reagents were used without any purification. They include: 2-hydroxyl-1-naphthaldehyde, 2-nitroaniline, ruthenium chloride hexahydrate, methanol, ethanol, diethyl ether, ethyl acetate, chloroform, dichloromethane, hexane, dimethyl sulfoxide, dimethylformamide, acetone and tetrahydrofuran.

procedure for the synthesis of the ligands (HL1 and HL2)

The Schiff base ligands HL1 and HL2 were synthesized according to modified literature procedures (10 Fugu, *et al.*, 2013). 2-hydroxy-1-naphthaldehyde (5 mmol, 0.86 g) was weighed and dissolved in 20 ml of ethanol. The ethanolic solution was mixed with each of the selected amines: 2-aminophenol (5 mmol, 0.545 g) and 2-nitroaniline (5 mmol, 0.691g), in 20 ml of methanol respectively, followed by the addition of 3 drops of conc. H₂SO₄. The mixture was refluxed for about 3-4 hours at room temperature. The product obtained was washed with diethyl ether. Followed by drying in a desiccator over fused calcium chloride (CaCl₂). This gave the Schiff base ligands: HL1-HL2.

General procedure for the synthesis of the metal complexes

The complexes were prepared using 1:1 mole ratio of metal to ligand following a standard procedure (Fugu, *et al.*, 2013 and Naureen, *et al.*, 2021). RuCl₃·6H₂O (1 mmol, 0.225 g) was weighed and dissolved in 20 ml of methanol and mixed with 20 ml methanolic solution of HL1 and HL2. The mixture was refluxed for about 3 hours using a hot plate magnetic stirrer. The product obtained was filtered and washed with an appropriate solvent and dried over fused CaCl₂ in a desiccator.

Measurements

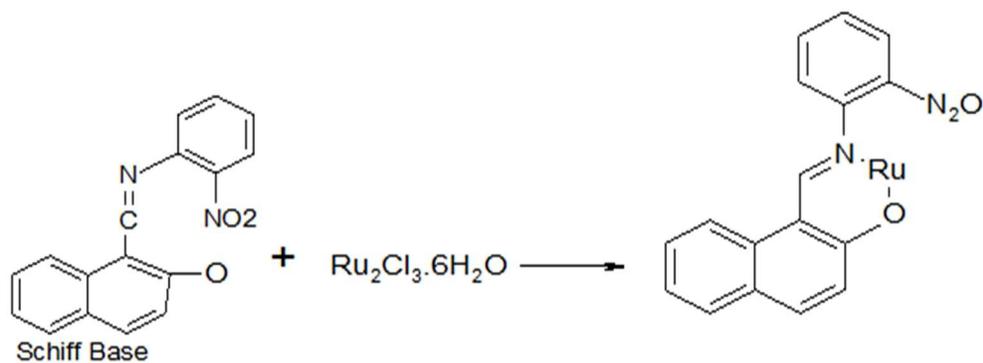
The synthesized compounds were subjected to physical and spectroscopic analyses to confirm their formation. These include ¹H NMR, ¹³CNMR, FTIR, UV-Visible, Elemental-CHN analysis and Metal analysis. The ¹H and ¹³C{H}NMR spectra were recorded on Bruker 500 MHz and 125 MHz, respectively. The Infrared spectral data were obtained using Tensor 27 Bruker and Perking Elmer FT-IR spectrometer BX. The elemental content (CHN) of the ligand and their complexes was obtained using VarioElementar III microbe CHN analyser. All NMR analyses were conducted at room temperature, and the chemical shifts are reported as parts per million (ppm) relative to tetra methyl silane which is used as internal standards for ¹H NMR and ¹³C NMR in DMSO-d₆.

RESULTS AND DISCUSSION

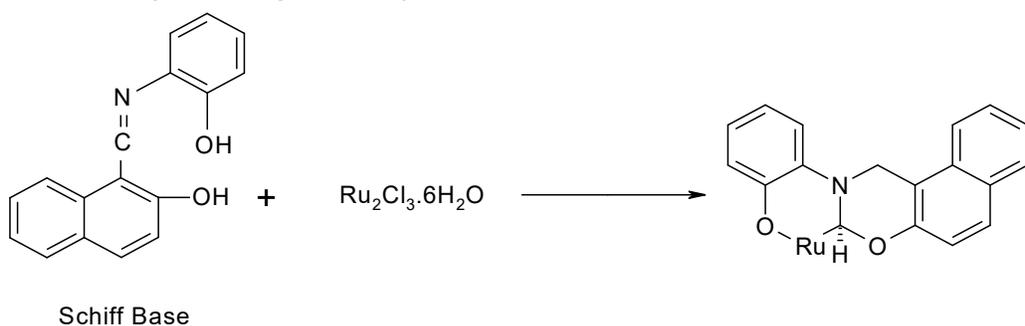
The Schiff base ligands HL1 and HL2 were synthesized via condensation of 2-aminophenol and 2-hydroxy-1-naphthaldehyde in 1:1 mole ratio, using methanol as a solvent.

The Schiff bases were obtained as yellow and red powders respectively, they are air and moisture stable, soluble in polar solvents but insoluble in non-polar solvents. However, the intensity of the colors varies and could be due to the influence of the chromophore groups. The metal complexes were obtained by the reaction of the Schiff bases with RuCl₃·6H₂O in 1:1 mole ratio at a room temperature. The complexes were obtained in moderate yield as black shiny solids; no variation of color intensity was observed on the complexes. They are soluble in methanol, ethanol, DMSO, DMF and water, but insoluble in chloroform, dichloromethane and non-polar solvents. The solubility of the complexes in polar solvents suggested that they probably polar complexes. The molar conductivity measurement of solution of the complexes in (methanol, 10⁻³M) was found to be 9.42 and 8.63 Ω⁻¹ cm² mol⁻¹, suggesting non-electrolytic complexes. The ligands and their complexes were characterized using spectroscopic analysis such as ¹H NMR, ¹³CNMR, FTIR, UV-Visible, and Elemental analysis. The data obtained from the elemental analysis (CHN) on the

ligands and their complexes correlate well with stoichiometric composition of the compounds and are in good agreement with the theoretical values. The physico-chemical and analytical data of the ligands and complexes are presented in Table 1.



Scheme 3: Synthesis of the complex HL2Ru



Scheme 4: Synthesis of the complex HL1Ru

Table 1: Physico-chemical properties of the ligands and their complexes

Cpd	Molecular formula (Molecular weight)	Color	Yield % (g)	m.p./d.p (°C)	Elemental analysis:				Molar conductivity ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)
					Cal (found)			Ru	
					C	H	N		
HL1	C ₁₇ H ₁₃ NO ₂ (263)	Yellow	80 (0.6)	200-201	77.56 (77.45)	4.9 (4.6)	5.3 (5.1)	-	-
HL2	C ₁₇ H ₁₂ N ₂ O ₃ (292)	Red	74 (0.65)	192-193	69.86 (69.82)	4.10 (4.08)	9.58 (9.08)	-	-
[HL1Ru]	RuC ₁₇ H ₁₃ NO ₂ (364)	Black	76 (1.60)	242-243	56 (55.1)	3.57 (3.41)	3.85 (3.21)	27.7 (27.6)	17x10 ⁻³
[HL2Ru]	RuC ₁₇ H ₁₂ N ₂ O ₃ (393)	Black	78 (1.50)	246-248	51.9 (50.9)	3.1 (3.1)	7.12 (6.99)	25.6 (25.2)	13x10 ⁻³

m.p. = Melting point; d.p. = Decomposition point; Calc. = Calculated; g = Grams

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

Nuclear magnetic resonance (NMR) spectroscopy is one of the vital tools that are used in structural elucidations. It is used to ascertain how atoms and molecules within a particular compound are related. This is achieved by analyzing chemical domain of the selected nucleus. To establish the formation of the compounds and also to elucidate their structure, the ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the ligands and the magnetic Ru(III) complexes were recorded in DMSO- d_6 . The spectra of both the ligands and their complexes showed different peaks that were characteristics of the compounds. Furthermore, both the spectra of HL1 and HL2 presented peaks in a similar chemical environment. A weak single peak at 1.04 and 0.86 ppm in the ligands is due to the $-\text{NH}$ proton of the Schiff base ligands in HL1 and HL2 respectively. The appearance of this proton in the downfield region is an indication of its involvement in intra-molecular hydrogen bonding with the nitrogen of the amine group. This is because hydrogen bonding often lowered the electron density around the proton, and hence moves the absorption of the proton to the downfield. Similarly, the phenolic protons of ligands were observed at 6.75 and 6.53 ppm as a sharp doublet peak and triplet peaks respectively. These protons appeared in downfield region due to the electronegative effect of oxygen atom, which causes the proton to be de-shielded and subsequently occurred in the downfield region. The azomethine proton ($\text{HC}=\text{N}$) signals were observed at 3.36 and 2.41 ppm in the two ligands respectively. This peak appeared downfield as in usual azomethine proton in Schiff bases. The chemical shifts of the aromatic protons in both ligands were observed within 7.09 –8.90 ppm. There is also appearance of single sharp peak at 10.31 and 10.77 ppm in the two spectrums, which is due to the moisture (water) in the DMSO- d_6 that was used for the NMR.

The aromatic carbon that is directly linked to the phenolic oxygen ($\text{C}-\text{OH}$) was observed in the downfield region at 178 ppm in HL1 and 193.4 ppm in HL2 (Figures 1-2). In the same manner, the azomethine ($\text{HC}=\text{N}$) carbon of HL1 was observed at 149.80 and 146.99 in HL2 were the aromatic carbons were obtained around 108.4-138.3 ppm in HL1 and 110 – 138.3 ppm in HL2 ligand(Figures below)

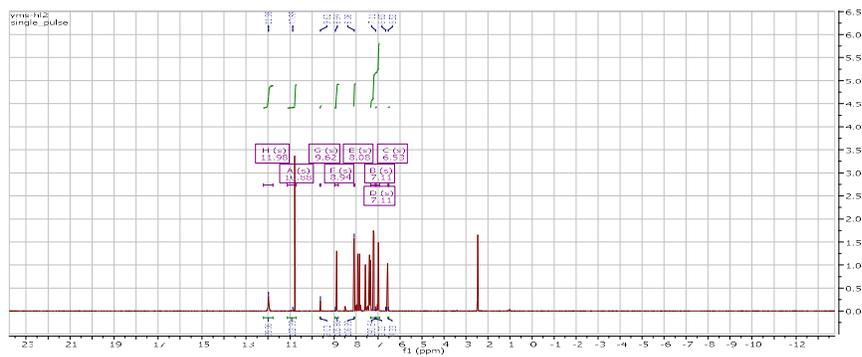


Figure 4: ¹H NMR spectrum of HL2 (DMSO-d₆)

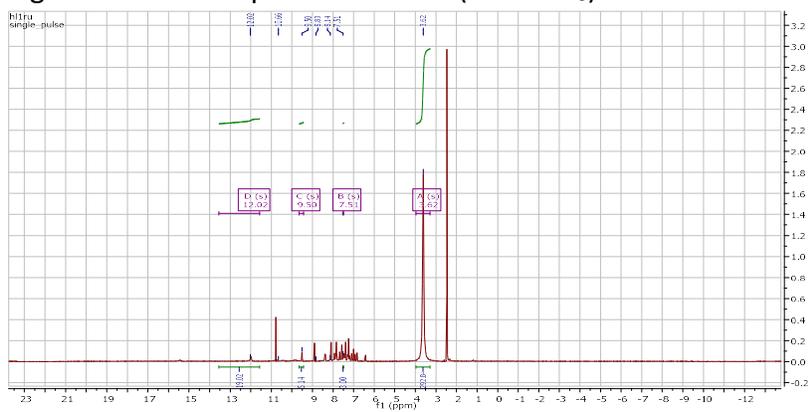


Figure 5: ¹H NMR spectrum of HL1Ru (DMSO-d₆)

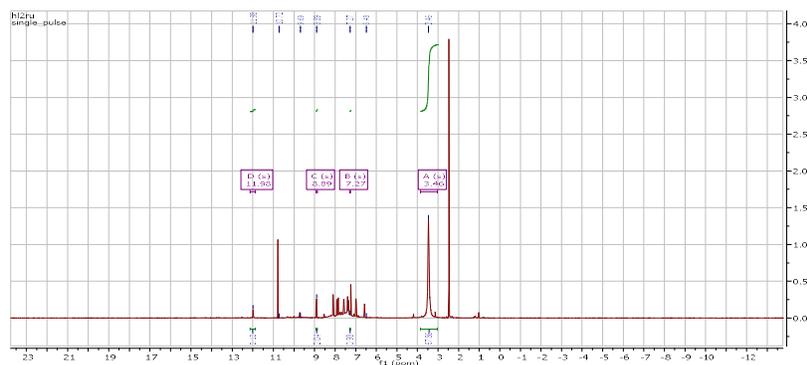


Figure 6: ^1H NMR spectrum of HL2Ru (DMSO- d_6)

After coordination to the Ru(III) ion, as seen from the ^1H NMR spectra of the complexes (Figures 5-6). The $-\text{NH}$ and $-\text{OH}$ protons that appeared downfield in the free ligands did not appear on the spectra of the complexes. The disappearance of these protons in the complexes confirmed the deprotonation of the protons, and coordination of the Ru(III) ion to the ligand through oxygen atom of the hydroxyl and the nitrogen atom of the azomethine groups. Similarly, the deprotonation of the proton further affirmed the existence of bonding between the oxygen atom of the hydroxyl ion and the Ru(III). In addition, the azomethine and the aromatic protons were significantly shifted in the complexes (Figures 5-6). The shift in the chemical environment of the azomethine proton is due to the involvement of the nitrogen atom in the coordination. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the complexes, showed insignificant shift toward any region for (C-OH) and (HC=N) carbons. This shifts, confirmed that, the Ru(III) ion are paramagnetic in nature this is as a result of unpaired electrons in their d-orbital (Waziri, *et al.*, 2022).

Infrared spectroscopy

plays a vital role in coordination chemistry, and it is one of characterization techniques that are used to confirm the formation of complex between ligands and metal ions. In order to verify the formation of complex, the infrared spectrum of ligand is compared with that of the complex. Herein, the infrared spectra of the ligands and their complexes were obtained in the region of $3500 - 500 \text{ cm}^{-1}$. The data for some selected stretching bands are presented in Table 2. The spectra of the ligands showed a sharp and weak intensities bands at 1546.75 and 3119.15 cm^{-1} for HL1 and sharp and medium intensities at 1509.0 - 3473.0 cm^{-1} for HL2, which are assignable to $-\text{NH}$ and $-\text{OH}$ characteristic bands. The appearance of new band in all the complexes in region of 617 cm^{-1} which are assignable to metal-oxygen band as reported in the literature (Ashrafuzzaman, *et al.*, and Refat, *et al.*, 2021) further confirmed the formation of the complexes.

A sharp stretching band at 1616 and 1620 cm^{-1} are due to imine (C=N) band of the azomethine moieties within the ligands HL1 and HL2 (Table 2). This band is the key indicator for the formation of Schiff bases (Savcı, *et al.*, 2021 and Suryawanshi, *et al.*, 2014). The bands shifted to lower frequency of (1612–1613) cm^{-1} on the spectra of the complexes. The shift to the lower frequency upon complexation and subsequent formation of new sharp bands at 561 and 529 cm^{-1} are due to metal-nitrogen band, confirmed the involvement of the azomethine nitrogen in the complexation. The sharp bands were observed at 861 and 827 cm^{-1} in the two complexes of HL1Ru and HL2Ru. The shifts in these bands are as a result of the vibration within the molecules arising from complexation.

Table 2: Infrared spectral data of the ligands and their complexes

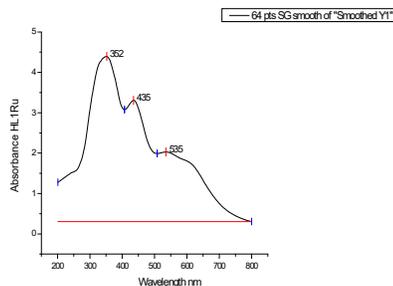
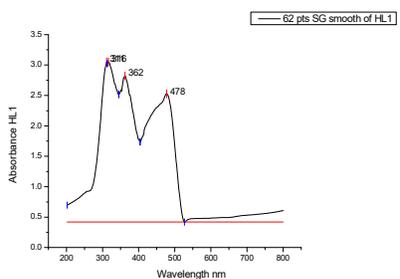
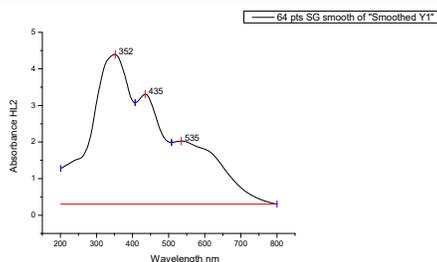
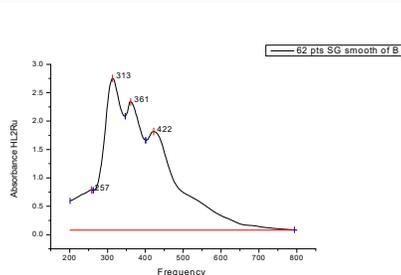
compound	$\nu(\text{O-phenolic})$	$\nu(\text{N-H})$	$\nu(\text{HC=N})$	Ru-N	Ru-O
HL1	3413	1509	1616	-	-
HL2	3119	1546	1620	-	-
HL1Ru	3411	1593	1612	561	600
HL2Ru	3451	1596	1613	529	694

Electronic spectral study

To establish the formation of the complexes, electronic spectral study was carried out on the free ligands and their complexes in DMSO (10^{-3}M). The spectra of the ligands displayed absorption bands at 314–361 nm and 316–361 nm respectively. These peaks can be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ within the aromatic moiety and azomethine group respectively (Abbas, 2016). On complexation, these bands shifted to lower wavelength at 352–535 nm and 313–422 nm respectively. These bands are assignable to charge transfer transition of the type $\text{O}(\rho\pi) \rightarrow \text{Ru}(d\pi)$ and $\text{N}(\rho\pi) \rightarrow \text{Ru}(d\pi)$, respectively due to the ON donor ligands system in a tetrahedral geometry. (Cui, *et al.*, 2016). Furthermore, Ru(III) complexes with tetrahedral geometry experienced orbital splitting pattern of $d_{x^2-y^2}$ and d_{z^2} with low orbital energy as the result of the orbital between the ligand axis experiences little repulsion.

Table 3: Electronic spectral data of the ligands and their complexes

compounds	λ max (nm)	Band assignment	Geometry
HL1	314	$\pi \rightarrow \pi^*$	-
	361	$n \rightarrow \pi$	
HL2	320	$\pi \rightarrow \pi^*$	-
	361	$n \rightarrow \pi^*$	
HL1Ru	352	$n \rightarrow \pi^*$	Tetrahedral
	535	LMCT	
HL2Ru	313	$n \rightarrow \pi^*$	Tetrahedral
	422	LMCT	



CONCLUSION

The Ru(III) metal complexes were synthesized from two Schiff base ligands. The ligands and their complexes were characterized using various characterization techniques. The characterization techniques, include the spectroscopic analysis such as the IR, UV- Visible, ^1H and ^{13}C NMR spectroscopy and elemental analysis (CHN). Formation of the ligands and their complexes was confirmed by the spectroscopic techniques and other physicochemical properties such as colour change, conductivity values, molecular weight of the compounds and their melting point values.

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