

Synthesis and Characterization of ethoxy salal thiosemicarbazone ruthenium(III) complexes

K. Sampath¹, KN. Thirumalaivasan²

¹Department of Chemistry, School of Foundational Sciences, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India.

²Department of Electronics and Instrumentation Engineering, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India

Abstract - Thiosemicarbazones have garnered significant attention in scientific research due to their valuable properties as ligands, including optical, antibacterial, antifungal, anticancer activities, and more. By integrating these bioactive ligands with active metals, novel compounds with diverse properties can be synthesized. Bearing this in mind, we carried out a study to prepare ruthenium complexes using thiosemicarbazone ligands substituted with end substitution. Through characterization, we determined that the resulting ruthenium complexes exhibit an octahedral geometry, as revealed by our investigation.

Key Words: Ruthenium, salal derivatives, spectroscopy, end substitution, ligand substitution.

1. INTRODUCTION

The synthesis and characterization of ruthenium Schiff base complexes have gained considerable attention in recent years due to their significant potential in various fields of chemistry, including catalysis, materials science, and bioinorganic chemistry. Schiff base complexes are formed by the coordination of a metal center, such as ruthenium, with a Schiff base ligand. The Schiff base ligand is typically derived from the condensation reaction between an aldehyde and an amine.

The synthesis of ruthenium Schiff base complexes involves the careful selection of appropriate ligand components and reaction conditions. The choice of aldehyde and amine precursors allows for the customization of the electronic, steric, and functional properties of the resulting complexes [1] [2]. The reaction is typically conducted under inert atmosphere conditions using suitable solvents and moderate temperatures.

Thiosemicarbazone ligands are a class of versatile molecules that have gained significant attention in coordination chemistry. These ligands possess a thiosemicarbazone functional group, which consists of a thioamide (-C=S) and a hydrazine (-NH-NH₂) moiety [3] [4]. Thiosemicarbazone ligands offer a diverse range of coordination possibilities due to the presence of different substituents on the parent thiosemicarbazone backbone. These substituents can be modified to incorporate various

functional groups, allowing for fine-tuning of the ligand's electronic and steric properties [5]. Thiosemicarbazone ligands have demonstrated promising applications in the development of metal-based complexes for catalysis, bioinorganic chemistry, and medicinal chemistry [6] [7]. Their ability to form stable complexes with various metal ions makes them valuable tools for designing new materials and exploring their potential in different fields of research.

Characterization techniques play a crucial role in understanding the structural and electronic properties of ruthenium Schiff base complexes. Elemental analysis provides information about the elemental composition of the complex, verifying the presence of ruthenium and other atoms within the complex. Spectroscopic techniques such as UV-Vis, and Infrared spectroscopy are employed to study the electronic transitions and vibrational modes of the complexes. These spectroscopic methods offer valuable insights into the bonding, coordination geometry, and electronic structure of the complexes [8] [9].

In summary, the synthesis and characterization of ruthenium Schiff base complexes offer a fascinating avenue for exploring their structural, electronic, and reactivity properties. These studies contribute to the development of novel catalysts, functional materials, and bioinorganic systems with diverse applications in various scientific disciplines.

2. EXPERIMENTAL

All chemicals utilized in the study were of analytical reagent (AR) grade, and the solvents were purified and dried with standard procedures. The synthesis of metal starting complexes, [RuCl₃(PPh₃)₃], [RuCl₃(AsPh₃)₃], and Schiff base ligands are shown below. Elemental analyses (C, H, N & S) were conducted using a Vario EL III CHNS analyzer at STIC, Cochin University of Science and Technology, Kerala, India. IR and Magnetic moment values are recorded in our research laboratory.

2.1 Synthesis of sample ligand

The ligand sample was prepared following the procedures described in prior published literature [9]. 3-

ethoxysalicylaldehyde and thiosemicarbazide, in a 1:1 molar ratio, were combined in ethanol and methanol, respectively, under continuous stirring for one hour. As a result, a white precipitate was formed, which was subsequently filtered. The structure of the sample ligand is shown in Fig.1.

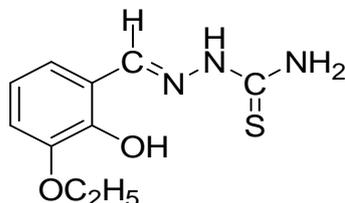


Fig.1. Ligand Structure

2.2 Synthesis of starting ruthenium metal complexes, $[\text{RuCl}_3(\text{PPh}_3)_3]$

The initial ruthenium metal complex, $[\text{RuCl}_3(\text{PPh}_3)_3]$, was synthesized following the documented literature [10]. Ethanol was used as the solvent for ruthenium trichloride trihydrate (1 mmol), to which concentrated hydrochloric acid was added. Triphenylphosphine (3 mmol) was subsequently introduced into the solution. The mixture was then refluxed for approximately five minutes and allowed to cool. The resulting crystals, which exhibited a reddish-brown color, were isolated, washed with ether, and subsequently dried. The structure of the starting triphenylphosphine ruthenium complex is shown in Fig.2.

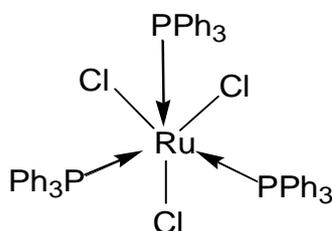


Fig.2. The structure of the $[\text{RuCl}_3(\text{PPh}_3)_3]$

2.3 Synthesis of starting ruthenium metal complexes, $[\text{RuCl}_3(\text{AsPh}_3)_3]$

The initial ruthenium metal complex, $[\text{RuCl}_3(\text{PPh}_3)_3]$, was synthesized following the documented literature [11]. Methanol was used as the solvent for ruthenium trichloride trihydrate (1 mmol), and concentrated hydrochloric acid was added to the mixture. The resulting solution was subjected to reflux for a duration of thirty minutes. Following this, triphenylarsine (3 mmol) in methanol was introduced and refluxed for an additional thirty minutes. The resulting oily substance was transferred to a mortar and left to air dry. Once dry, it was crushed using a pestle. The resulting material was washed with methanol and subsequently dried under vacuum. The structure of the starting triphenylarsine ruthenium complex is shown in Fig.3.

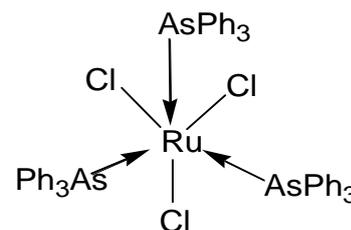


Fig.2. The structure of the $[\text{RuCl}_3(\text{AsPh}_3)_3]$

2.4 Synthesis of sample complexes

Equal mole ratios (0.5 mmol) of the ligand and the initial ruthenium complexes are dissolved separately in methanol and toluene. Subsequently, the solutions are subjected to reflux for approximately 11 hours and then allowed to cool. This process leads to the formation of vibrant precipitates, which are subsequently filtered.

3. RESULTS AND DISCUSSION

TABLE 1. Analytical details of ligand and complexes

Complexes	Color	Elemental analysis calculated (Found) %			
		C	H	N	S
(PPh ₃) complex	Light Yellow	61.50 (62.09)	4.60 (4.86)	4.68 (4.77)	3.57 (4.01)
(AsPh ₃) complex	Orange	56.02 (55.67)	4.19 (3.95)	4.26 (4.81)	3.25 (3.88)

Table 1 presents the analytical data for both the ligand and the complexes, while the spectroscopic data provides insights into their characteristics. Notably, the analysis reveals a 1:1 metal-ligand stoichiometry. It is worth mentioning that the synthesized complexes demonstrate a non-hygroscopic nature. For a better understanding, the synthesis process and the proposed structure of the complexes are depicted in the above scheme.

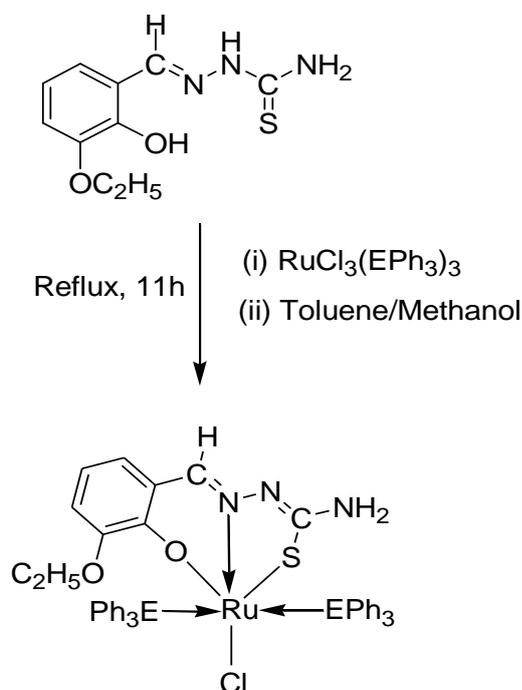
3.1 Infra-Red

To determine the binding mode of the Schiff base ligand in the complexes, the most significant IR spectral frequencies of the complexes (Table-2) were compared with those of the ligand. The complexes exhibited an azomethine C=N stretching frequency at 1615-1929 cm^{-1} , which was lower than that of the free ligand (1621 cm^{-1}) [12]. This confirms that one of the binding modes of the Schiff base ligand with the ruthenium metal involves the azomethine nitrogen. The phenolic CO band of the complexes displayed a shift towards higher frequencies at 1241-1257 cm^{-1} compared to the free ligand (1240 cm^{-1}), indicating another coordination mode through C-O-M bonding. The C-S stretching frequency in the

complexes showed a lower frequency at 723-746 cm^{-1} compared to the ligand, suggesting coordination of the C-S to the ruthenium atom [13]. In summary, the Schiff base ligand acts as a monobasic tridentate ligand in the studied complexes.

TABLE 2. FT-IR spectral details of compounds

Ligand and Complexes	FT-IR, cm^{-1}			
	$\nu(\text{Ph-OH})$	$\nu(\text{C=N})$	$\nu(\text{Ph-CO})$	$\nu(\text{C-S})$
Ligand	1222	1639	-	957
(PPh_3) complex	-	1629	1241	723
(AsPh_3) complex	-	1615	1257	746



SCHEME 1. Synthesis of complexes, E=P/As

3.2 Electronic Spectra

TABLE 3. Electronic spectral data of compounds

Ligand and Complexes	λ_{max} (nm)
Ligand	302, 383
(PPh_3) complex	309, 394, 427
(AsPh_3) complex	309, 392, 421

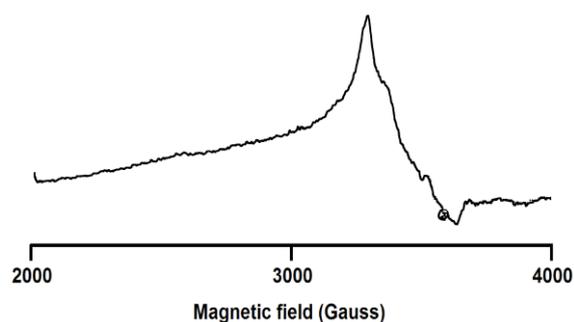
The electronic spectra of the complexes (Table-3) were recorded using DMSO as the solvent. The complexes displayed three bands within the range of 309-427 nm. The shifts observed in the ligand-centered transitions at 309-394 nm confirmed the coordination of the Schiff base ligand (308-420 nm) to the ruthenium atom [13]. Consequently, assigning the bands appearing in the visible region becomes challenging. Hence, the bands observed at 421-427 nm have been attributed to charge transfer transitions, which align well with similar reported ruthenium(III) complexes [14].

3.3 Magnetic moment measurements

Both ruthenium(III) complexes exhibited a magnetic moment value of $\mu_B = 1.39$ (PPh_3) and 1.41 (AsPh_3) at room temperature, indicating their paramagnetic nature. This observation corresponds to the presence of an unpaired electron in a low-spin $4d^5$ configuration, confirming the +3 oxidation state of ruthenium [15].

3.4 EPR spectra

The room temperature EPR spectra of the powdered complexes were documented in the X-band (figure 3), without displaying any hyperfine splitting due to interactions with other nuclei within the complexes. A single isotropic resonance was observed, with g values, 2.35 (PPh_3) and 2.49 (AsPh_3) [14]. Although the complexes exhibited slight distortion in their octahedral geometries, the presence of isotropic lines in the EPR spectra indicates that the unpaired electron occupies a degenerate orbital. The obtained EPR spectra are in accordance with ruthenium complexes previously reported [15].


 Fig 3. EPR Spectrum of PPh_3 complex

3. CONCLUSIONS

The investigation focused on synthesizing and characterizing ruthenium complexes utilizing the ethoxy salal thiosemicarbazone ligand and ruthenium starters. To characterize both the ligand and its complexes, elemental analysis and a variety of spectroscopic techniques were employed. The analysis of the spectra revealed that the derived ruthenium complexes exhibit an oxidation state of +3. The ethoxy salal thiosemicarbazone ligand binds to

ruthenium in an SNO manner, providing confirmation of the octahedral geometry observed in the complexes investigated during this study.

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