

SYNTHESIS AND CHARACTERIZATION OF RUTHENIUM (III) COMPLEXES WITH TRIDENTATE (ONO) SCHIFF BASES

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Abstract

The reactions of Ru(III) chloride with tridentate dibasic Schiff bases (H₂SB) gave anionic complexes of types [Ru(SB)₂]⁻(Et)₄N⁺. Schiff bases prepared from salicylaldehyde, 5-chlorosalicylaldehyde, and 5-bromosalicylaldehyde with 2-aminophenol. The anionic complexes have been prepared and precipitated with tetraethylammoniumbromide. New complexes have been characterized based on elemental analyses, IR spectroscopy, UV-VIS spectroscopy, and ESI mass spectrometry. Measures of mass spectrometry with the method ESI show that the complexes are anionic and the calculated molecular mass of the corresponding anion complies with the molecular mass of the experimentally found complex anion. The results are in accord with an octahedral environment around the Ru (III) ion.

Keywords: Ruthenium complexes, Schiff bases, spectroscopy studies, ESI mass spectrometry

1. Introduction

For several decades Schiff bases and their metal complexes have been attracting special interest due to its potential anti-viral, anti-fungal, and anti-tumor properties [Smith and Read]. Many metal complexes with various Schiff bases have been intensively studied mostly because of their pharmaceutical and biochemical importance. On the other hand, some ruthenium complexes have shown promising anticancer activity and have been continuously investigated as the most important non-Platinum based anticancer candidates in clinical trials [Mestroni et al, 1993; Clarke et al, 2003; Galanski et al, 2003; Alessio et al, 2004]. Reported that Tetraethylammoniumdichloro-bis[N-phenyl-5-chlorosalicylideneiminato-N, O]ruthenat(III) can be used as a new amperometric sensor for ascorbic acid determination [Kahrović et al, 2012].

Our work is based on the synthesis of the dibasic tridentate (ONO) Schiff bases with general formula H₂SB, which can be coordinated with ruthenium(III) ion through two O atoms and one N atom. The ruthenium ions(III) formed complexes with tridentate dibasic Schiff bases in the 1:2 ratio. For deprotonated of the phenol groups, it is used triethylamine. Precipitation of the complexes is made with tetraethylammoniumbromide.

2. Experimental

2.1. *Materials and methods:* All chemicals were purchased from commercial sources and used without further purification. The infrared spectra were recorded as KBr pellets on a Perkin Elmer spectrum BX FTIR System. UV-Vis spectra were measured on the Jasco V-670 spectrophotometer. Elemental analyses were performed on a Vario EL analyzer. ESI-MS spectra were recorded on FT-ICR-MS Bruker Daltonics.

2.2. *Preparation of the Schiff Bases:* The ligands, salicylidene 2-aminophenol, 5-chlorosalicylidene-2-aminophenol, 5-bromosalicylidene-2-aminophenol was synthesized by adding an absolute ethanolic solution of corresponding salicylaldehyde to an absolute ethanolic solution of 2-aminophenol in 1:1 ratio followed by refluxing for 20 min in 65°C. On cooling, a colored product was obtained which was filtered and recrystallized with absolute ethanol.

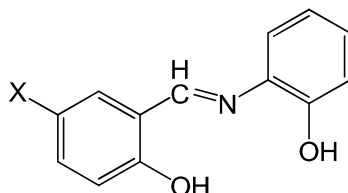
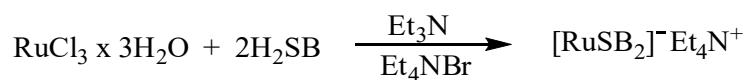


Figure 1. Salicylidene-2-aminophenol

2.3. *Preparation of the complexes:* Measured 1mmol $\text{RuCl}_3 \times 3\text{H}_2\text{O}$ (0,261g) and solved in 10 ml absolute ethanol. Also, measured 2mmol of the Schiff base and solved in 40 ml absolute ethanol heated with stirring and was added 0,6 ml triethylamine. Then the Schiff base added carefully dropwise in the ruthenium solution and refluxed for two hours on a paraffin oil bath. After refluxing, the reaction mixture cooled in room temperature and slow evaporated to 30 ml. To this solution is added in excess tetraethylammoniumbromide solved in minimum water, a dark green precipitate is formed, filtered, and washed with petroleum ether and cyclohexane.

3. Results and discussion

The data of elemental analysis suggests that the complexes have 1:2 (Ru-SB) stoichiometry. Considerate that the Schiff bases are dibasic and tridentate, the formed complexes are anionic and have octahedral structure. In the presence of triethylamine is made deprotonated of phenol groups of the Schiff bases and in this way, they become strong tridentate ligands. The general equation for the synthesis of the ruthenium complexes can be shown:



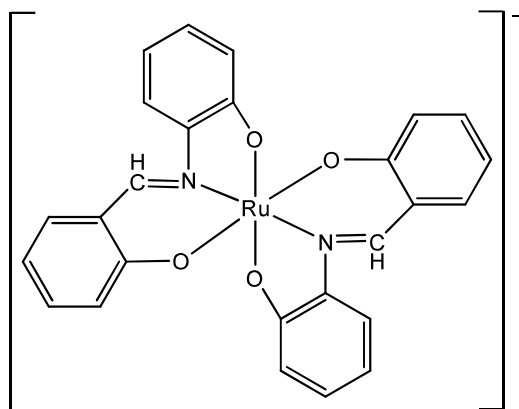


Figure 2. Suggested structure of anion complex $[\text{Ru}(\text{SB}^{\text{I}})_2]^-$

3.1. IR Spectroscopy: If it is compared to the IR spectra of ligands and the complexes it can be noticed that the stretching band of the C=N group is shifted to lower frequencies. Thus, at the free ligand $\text{H}_2\text{SB}^{\text{I}}$ this group absorbs at 1633 cm^{-1} while the complex is showing a band at 1595 cm^{-1} . Similarly, the ligand $\text{H}_2\text{SB}^{\text{II}}$ absorbs at 1630 cm^{-1} and the complex at 1590 cm^{-1} . Finally, a band at 1630 cm^{-1} was noticed due to the vibrations of the C=N group at $\text{H}_2\text{SB}^{\text{III}}$, and in the complex, this band was shifted to 1597 cm^{-1} . The shifting of the band is very normal and it is a consequence of the coordination of Nitrogen of the C=N group with the ion of Ruthenium (Mishra et al, 2002). In the IR spectra of the ligands, the C-O stretching band at 1245 cm^{-1} was noticed. The complexes were showing bands of this vibration at higher energy, at 1257 cm^{-1} ($\pm 12\text{ cm}^{-1}$). These phenomena are explained by the deprotonation of the phenol groups and by chelating with the ion of Ruthenium (Mishra et al, 2002). The presence of lonely stretching vibrations at 1360 cm^{-1} at the three complexes which is not present at ligands is devoted to C-N bonds of tetraethylammonium cations (Coates J, 2000). The presence of Ru-O bonds is shown by the appearance of Ru-O stretching vibrations at 540 cm^{-1} (Demir et al, 2008). Finally, the stretching vibrations of Ru-N bonds were detected at $420\text{-}425\text{ cm}^{-1}$ (Sharma et al, 2006)

Table 1. Infrared Spectra of the Ruthenium(III) Complexes

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}-\text{N})$	$\nu(\text{Ru}-\text{O})$	$\nu(\text{Ru}-\text{N})$
$\text{H}_2\text{SB}^{\text{I}}$	1633	1245	/	/	/
$[\text{Ru}(\text{SB}^{\text{I}})_2]^- (\text{Et})_4\text{N}^+$	1595	1258	1358	539	422
$\text{H}_2\text{SB}^{\text{II}}$	1630	1245	/	/	/
$[\text{Ru}(\text{SB}^{\text{II}})_2]^- (\text{Et})_4\text{N}^+$	1590	1257	1364	540	425
$\text{H}_2\text{SB}^{\text{III}}$	1630	1245	/	/	/
$[\text{Ru}(\text{SB}^{\text{III}})_2]^- (\text{Et})_4\text{N}^+$	1597	1258	1362	539	424

3.2. UV-VIS Spectroscopy: The electronic spectra were recorded in the solution of chloroform in the region from 190-1600 nm. The data collected from the electronic spectra (table 2) of the complexes were suggesting the octahedral structure. The ground state of ruthenium (III) is $^2\text{T}_{2g}$, arising to the t_{2g}^5 configuration in an octahedral structure. The excited states are $^2\text{A}_{2g}$, $^2\text{T}_{1g}$, and $^2\text{E}_g$. In the octahedral coordinate ruthenium(III) complexes, charge transfer transition often occurs at relatively low energy (Chittilapilly et al, 2008). The intensive absorbance at 242-244 nm (λ_{lmax}) was

devoted to a π transition of the azomethine groups present in the complexes (Silverstein et al, 1991), as for as the phenyl groups also present (Böttcher et al, 1997). Absorbance at 408-414 nm was noticed due to ${}^2T_{2g} \rightarrow {}^2E_g$ transition (λ_{2max}) showing the octahedral structure of the ruthenium(III) ion (Chittilapilly et al, 2008).

Table 2. The data of UV-VIS spectra of the complexes

Compound	λ_{1max} (nm)	λ_{2max} (nm)
$[\text{Ru}(\text{SB}^{\text{I}})_2]^{-}(\text{Et})_4\text{N}^{+}$	242	408
$[\text{Ru}(\text{SB}^{\text{II}})_2]^{-}(\text{Et})_4\text{N}^{+}$	244	412
$[\text{Ru}(\text{SB}^{\text{III}})_2]^{-}(\text{Et})_4\text{N}^{+}$	244	414

3.3. Mass spectrometry: The mass spectra are measured using ESI (Electron Spray Ionization) negative method. Measured mass with this method in specters is shown only anion mass. The m/z measured values of anionic complexes are almost the same as theoretically calculated (table 3). The mass spectra of complexes are shown in figure 3,4,5.

Table 3. Mass spectra of the anion complexes (ESI anion mode)

m/z	$[\text{Ru}(\text{SB}^{\text{I}})_2]^{-}$	$[\text{Ru}(\text{SB}^{\text{II}})_2]^{-}$	$[\text{Ru}(\text{SB}^{\text{III}})_2]^{-}$
	$\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_4\text{Ru}^{-}$	$\text{C}_{26}\text{H}_{16}\text{Cl}_2\text{N}_2\text{O}_4\text{Ru}^{-}$	$\text{C}_{26}\text{H}_{16}\text{Br}_2\text{N}_2\text{O}_4\text{Ru}^{-}$
Found	524.03	591.96	681.85
Calculated	524.03	591.96	681.85

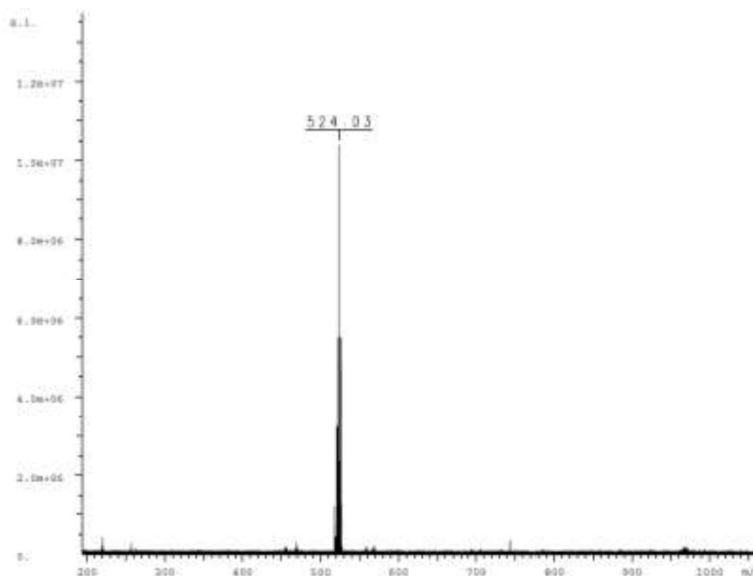


Figure 3. Mass spectra of $[\text{Ru}(\text{SB}^{\text{I}})_2]^{-}\text{Et}_4\text{N}^{+}$

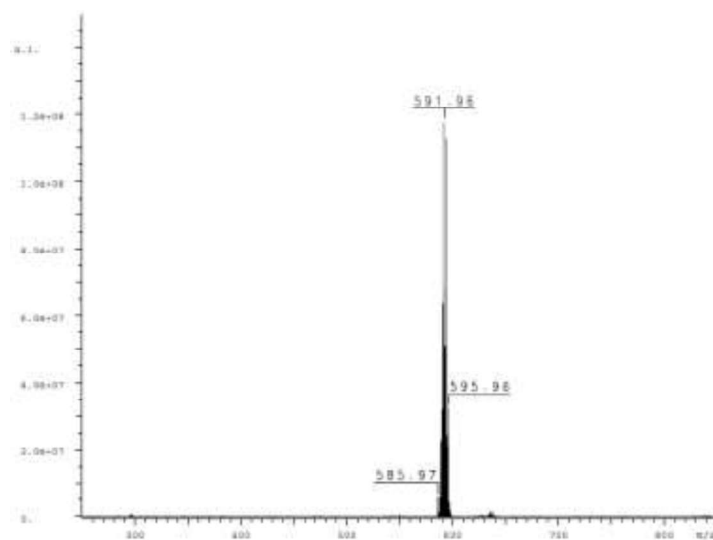


Figure 4. Mass spectra of $[\text{Ru}(\text{SB}^{\text{II}})_2]^+\text{Et}_4\text{N}^+$

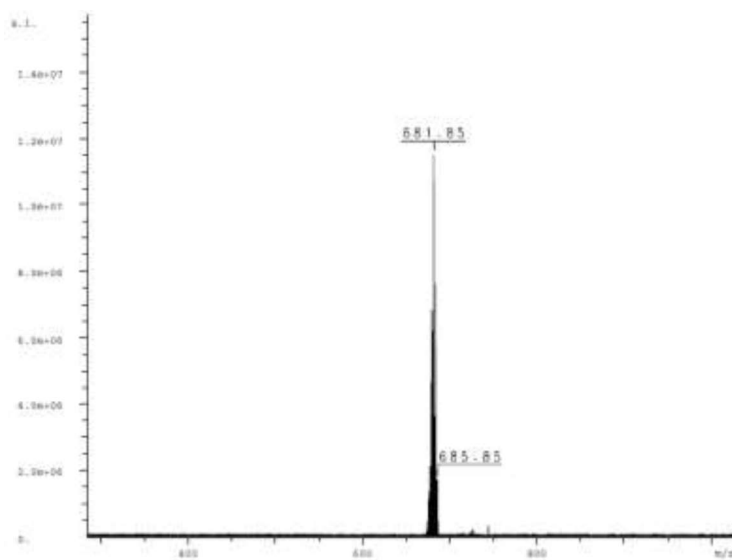


Figure 5. Mass spectra of $[\text{Ru}(\text{SB}^{\text{III}})_2]^+\text{Et}_4\text{N}^+$

4. Conclusion

The data of elemental analysis, IR spectra, UV-VIS spectra, and mass spectra show that tribasic Schiff bases (H_2SB) are coordinated with Ruthenium(III) ion and form Tetraethylammoniumbis[2-(2-hydroxybenzylideneamino)phenolate-O,N,O]ruthenat(III), Tetraethylammoniumbis[4-chloro-2-((2-hydroxyphenylimino)methyl)phenolate-O, N, O]ruthenat (III) and Tetraethylammoniumbis[4-bromo-2-((2-hydroxyphenylimino)methyl)phenolate-O,N,O]ruthenat (III). The Schiff bases are coordinated to the Ru(III) ion through two phenolic oxygens and azomethine nitrogen.

Nomenclature

H₂SB^I = salicylidene-2-aminophenol; H₂SB^{II} = 5-chlorosalicylidene-2-aminophenol, where X=Cl

H₂SB^{III} = 5-bromosalicylidene-2-aminophenol, where X=Br

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