

Spectrophotometric Characterization of the Complex Generated in Solution for the Reaction of H[Ru(III)Cl₂(H₂EDTA)] Complex with AETS Modifier Agent

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Abstract

Spectrophotometric method was used to evaluate the kinetic of the complex formation from the reaction between H[Ru(III)Cl₂(H₂EDTA)] and the modifier agent [3-(2-aminoethyl)aminopropyl]trimethoxysilane (AEATS) ($\mu = 0.50 \text{ mol}\cdot\text{dm}^{-3}$ with NaCF₃COO, 298.15 K), in pseudo-first order conditions. These studies showed that the reactions are successive producing several species influenced by the concentrations ratio. The electronics spectrum of all solutions showed a band in 457 nm with variable molar absorptivity (ϵ).

Keywords

[3-(2-Aminoethyl)aminopropyl]trimethoxysilane, H[Ru(III)Cl₂(H₂EDTA)] Complex, Spectrophotometric Method, Molar Absorptivity

1. Introduction

The examples in literature are abundant where complexes of Ru(III)/(II) containing organic ligands act as homogeneous catalysts [1]-[4].

The understanding of the alterations in chemical properties of the metallic center Ru(III)/Ru(II) and the coordinate ligand of the ethylenediamine type become important, and therefore examples in the literature of complexes with this ligand act as anti-inflammatory and anti-tumors [5] [6].

Complexes of Ru(III)-EDTA have been widely studied in function of its catalytic activity and as model of cytochrome P-450 [7] [8]. That makes the study of its sphere of coordination important that involves the metal-

lic center. These complexes of Ru(III)-EDTA are very sensible to the variations in the processes of synthesis and crystallization (pH, temperature and time of rest for the attainment of the product), presenting a very rich chemistry, with some products of synthesis [9].

In this work, the studied complex was dichloro(ethylenediaminetetraacetate)ruthenate (III) acid, $\text{H}[\text{Ru}(\text{III})\text{Cl}_2(\text{H}_2\text{EDTA})]$ (Figure 1), whose molecular structure recently was characterized by crystallographic data, being an anionic complex, with number of coordination six and approximately octahedral structure. The Ru(III) is linked to two chlorides in *cis*-position—two atoms of oxygen of the groupings carboxylates in position *trans* and two nitrogen atoms of the amino groupings of EDTA ligand.

EDTA ligand is linked to four positions to the Ru(III) ion and it forms chelate rings with two free carboxylate groupings. The positions of *trans* coordination in relation to nitrogen atoms are occupied by two chlorides. The lengths of Ru-Cl linkings are next to those told in literature [7] [9] [10]. The complex presents EDTA ligand with two carboxylates groupings in *trans* position. Two EDTA amino groupings with two chlorides (in *cis* position) complete the planar formation of the octahedral structure. In this conformation the chelate effect of EDTA ligand must facilitate the reactions of substitution of ligand in this complex.

This study is part of an ampler project, involving the $[\text{Ru}(\text{III})(\text{HEDTA})(\text{H}_2\text{O})]$ complex and its intermediary of synthesis $\text{H}[\text{Ru}(\text{III})\text{Cl}_2(\text{H}_2\text{EDTA})]$, and even so they are known for a long time, only the reactivity in solution of the $[\text{Ru}(\text{III})(\text{EDTA})(\text{H}_2\text{O})]^{1-}$ complex ion is well known [11]-[13] and its electrochemical behavior in modified chemically electrode has been studied [14] [15].

In literature [14], it found the study of the electrochemical behavior of the complex ion $[\text{Ru}(\text{III})(\text{EDTA})(\text{H}_2\text{O})]^{1-}$ adsorbed on modified silica with zirconium oxide (IV), as well as its electrocatalytic activity in the reduction of the oxygen.

In this work we describe the spectrofotometric study of the complex generated in solution for the reaction of the $\text{H}[\text{Ru}(\text{III})\text{Cl}_2(\text{H}_2\text{EDTA})]$ complex with AEATS modifier agent [3-(2-aminoethyl)aminopropyl]trimethoxysilane.

2. Experimental

2.1. Preparation of the $\text{H}[\text{Ru}(\text{III})\text{Cl}_2(\text{H}_2\text{EDTA})]$ Complex

It had been dissolved 10.0 g of ruthenium trichloride (Aldrich, P.A.) in 60.0 cm^3 concentrate HCl (Merck, P.A.), in a porcelain capsule, water bath and under agitation with a glass baton.

An orange solution was formed that was taken almost to the dryness. This process of evaporation was repeated many times, after 20.0 cm^3 addition of doubly-distilled water. It was added, then, 12.0 g of H_4EDTA (Carlo Erba), suspended in 10.0 cm^3 of water. It formed a viscose mass that was dissolved slowly by the addition of 60.0 cm^3 of concentrated HCl, under constant agitation. A precipitate was formed, dissolved, forming a dark oil that became an adherent mass. With the 20.0 cm^3 addition of water, it had redissolution, and the solution again was evaporated. This procedure was carried out many times. It was added then, 50.0 cm^3 of solution $6.0 \text{ mol}\cdot\text{dm}^{-3}$ of HCl. The solution was kept in freezer for three hours, having had the formation of a yellow solid. This solid, of composition $\text{H}[\text{Ru}(\text{III})\text{Cl}_2(\text{H}_2\text{EDTA})]$, was separated for filtration, washed with ether/ethanol mixture.

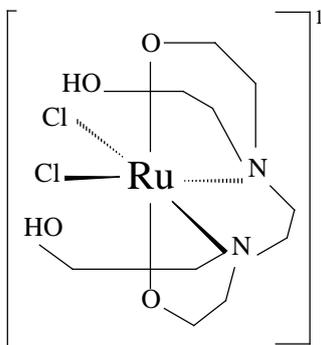


Figure 1. Molecular structure of the $\text{H}[\text{Ru}(\text{III})\text{Cl}_2(\text{H}_2\text{EDTA})]$ complex.

2.2. Characterization of the Complex Generated in Solution for the Reaction of H[Ru(III)Cl₂(H₂EDTA)] Complex with AETS Modifier Agent

2.2.1. Potentiometric Determination of Apparent pKas of the AEATS

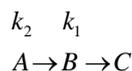
The solution of the AEATS was prepared (1.00×10^{-2} mol·dm⁻³, $\mu = 0.20$ mol·dm⁻³ adjusted with NaCF₃-COO), that she was titleholder with HCl (0.1002 mol·dm⁻³).

In the treatment of the data it had been used graphical method of derived first and second and also the Modified Gran Method [16].

2.2.2. Espectrofotometric Studied of the Solution 1.56×10^{-4} mol·dm⁻³ of H[Ru(III)Cl₂(H₂EDTA)] Complex with AEATS Modifier Agent

For the study of the kinetic one of formation a solution of the H[Ru(III)Cl₂(H₂EDTA)] complex (1.56×10^{-4} mol·dm⁻³) with AEATS modifier agent was prepared (0.35 and 0.50 mol·dm⁻³). The ionic force was adjusted (0.50 mol·dm⁻³ in NaCF₃COO, 298.15 K) and the electronic spectra had been gotten in the 235 - 800 nm region. It was also performed the kinetics of formation in ethanol to AEATS concentration of 0.20 mol·dm⁻³. The kinetic data could have been treating for computational methods, but the considered treatment was the graph for consecutive reactions of pseudo-first order [17], using Excell spread sheet and interactive method.

This treatment is described in literature [17], where two consecutive stages of first pseudo-order are considered:



and the following equations are used in this graphical method:

$$(A_f - A) = \alpha e^{(-k_1 t)} + \beta e^{(-k_2 t)} \quad (1)$$

$$\alpha = \frac{(\varepsilon_A - \varepsilon_B)k_1 + (\varepsilon_C - \varepsilon_A)k_2}{k_2 - k_1} [A]_o \quad (2)$$

$$\beta = \frac{(\varepsilon_B - \varepsilon_C)k_1}{k_2 - k_1} [A]_o \quad (3)$$

where A = absorbance, ε = molar absorptivity.

As foreseen for Equation (1), two segments of straight lines will be gotten in the graph $\ln(A_f - A)$ versus t (time) and, with the straight line referring to the slower kinetic the values of $k_{2\text{obs}}$ (angular coefficient) and $\ln\beta$ (linear coefficient) are obtained. The kinetic constant for the fast reaction is calculated using Equation (4) and considering $k_{1\text{obs}} > k_{2\text{obs}}$

$$\Delta = (A_f - A) - \beta e^{(-k_2 t)} = \alpha e^{(-k_1 t)} \quad (4)$$

$$\ln\Delta = \ln[(A_f - A) - \beta e^{(-k_2 t)}] = \ln\alpha - k_1 t \quad (5)$$

calling $-\beta e^{(-k_2 t)} = w$

$$\ln\Delta = \ln[(A_f - A) - w] = \ln\alpha - k_1 t \quad (6)$$

The amount $\ln[(A_f - A) - w]$ corresponds to the difference among the obtained values of the fast kinetic and the extrapolation of the linear portion of the slow kinetic.

Then $\ln[(A_f - A) - w]$ versus t (time) supplies another constant of speed $k_{1\text{obs}}$ (angular coefficient) and the value of $\ln\alpha$ (linear coefficient).

Therefore, the two constants are determined and, by Equation (3) the molar absorptivity (ε_B) of the intermediate B can be determined.

With all the definitive values ($k_{1\text{obs}}$, $k_{2\text{obs}}$, ε_A , ε_B and ε_C) the experimental confirmation of the kinetic data is effected applying Equation (7).

$$A_T = \varepsilon_A [A]_t + \varepsilon_B [B]_t + \varepsilon_C [C]_t \quad (7)$$

$$A_T = \varepsilon_A [A]_o + (\varepsilon_A - \varepsilon_C) [A]_o e^{(-k_1 t)} + (\varepsilon_B - \varepsilon_C) \frac{k_1 [A]_o}{k_2 - k_1} [e^{(-k_1 t)} - e^{(-k_2 t)}] \quad (8)$$

In this study of reactivity the relation in solution of the concentrations of ligand with the one of the complex was of 1282 (0.20 mol·dm⁻³ (ethanol)), 2244 (0.35 mol·dm⁻³) and 3205 (0.50 mol·dm⁻³), therefore always with great excess of ligand.

2.3. Characterization

The complex synthesized H[Ru(III)Cl₂(H₂EDTA)] was characterized by elemental analysis of carbon, nitrogen and hydrogen (Microanalysis Laboratory, USP).

The potentiometric measurements were performed in a pH meter/pot Digimed model DMPH-3. Temperature control was performed by a thermostat bath Microquímica, model MQBTZ 99-20.

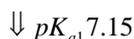
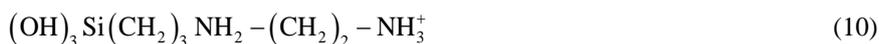
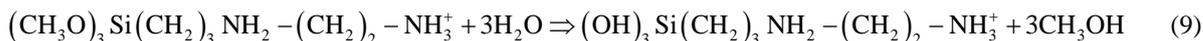
Microsyringes Gilmont Instruments were used in titrations, model GS-1200A, with a capacity of 2.000 cm³ and 0.002 cm³ of resolution, or 0.2000 cm³ 0.0002 cm³ with resolution and a magnetic stirrer Tecnal TE 085. Electronic spectra were made on double beam spectrophotometer UV-Vis GBC 918 coupled to a Cordata microcomputer, dual beam spectrophotometer UV-Vis Hitachi model U-2000 spectrophotometer and double beam spectrophotometer UV-Vis DU-70 using quartz buckets optical path of 1.0 and 0.1 cm.

3. Results and Discussion

Results of microanalysis complex H[Ru(III)Cl₂(H₂EDTA)] (calculated and experimental): (22.0% and 22.0%) C; (5.1% and 5.0%) N and (4.4% and 4.1%) H.

The above values are consistent with the complex, H[Ru(III)Cl₂(H₂EDTA) 4.5 H₂O.

The values of apparent pK_{as} for AETS were $pK_{a1} = 7.15 \pm 0.05$ and $pK_{a2} = 9.88 \pm 0.05$.



The electronic spectra of the reaction solution of the complex H[Ru(III)Cl₂(H₂EDTA)]: (1.56 × 10⁻⁴ mol·dm⁻³) with AEATS modified agent 12:35 mol·dm⁻³ (pH = 10.9) were registered according to the time, and they had the appearance of a band in the visible region $\lambda_{\text{max}} = 457 \text{ nm}$ ($\varepsilon_2 = 9.4 \times 10^3 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$) attributed to the charge transfer transition metal ligand, with isosbestic point at 395 nm, after five hours of reaction. The final spectrum was attributed to the H[Ru(III)Cl₂(H₂EDTA)] complex formed with AEATS modified agent coordinated bidentate to the metal. The formation kinetics were analyzed spectrophotometrically under pseudo-first order conditions, at 298.15 K, with $\mu = 0.50 \text{ mol} \cdot \text{dm}^{-3}$ (NaCF₃COO). The reaction of formation of the H[Ru(III)Cl₂(H₂EDTA)] complex with AEATS modified agent was slow and the wavelength chosen for the kinetic study was $\lambda_{\text{max}} = 457 \text{ nm}$.

The **Figure 2**, graph $\ln(A_f - A)$ versus time (s) is representative of the behavior observed in this system, with the obtaining of two lines, showing the existence of three species in solution involving two successive stages, with a competitive product, dependent on the pH and the relationship between the concentrations of the AEATS and complex.

The values of kinetic constants ($k_{2\text{obs}}$) were obtained by the slopes of the straight lines of the graphs of $\ln(A_f - A)$ versus time only for the slow step are shown in **Table 1**. The formation constants of the intermediates, $k_{1\text{obs}}$, giving graphic treatment successive reactions for this system were obtained by the graphs of $\ln[(A_f - A) - w]$ versus time (**Figure 3**) and are shown in **Table 1**.

The values of the molar absorptivity of the obtained product (ε_2) and intermediates (ε_1) as the starting

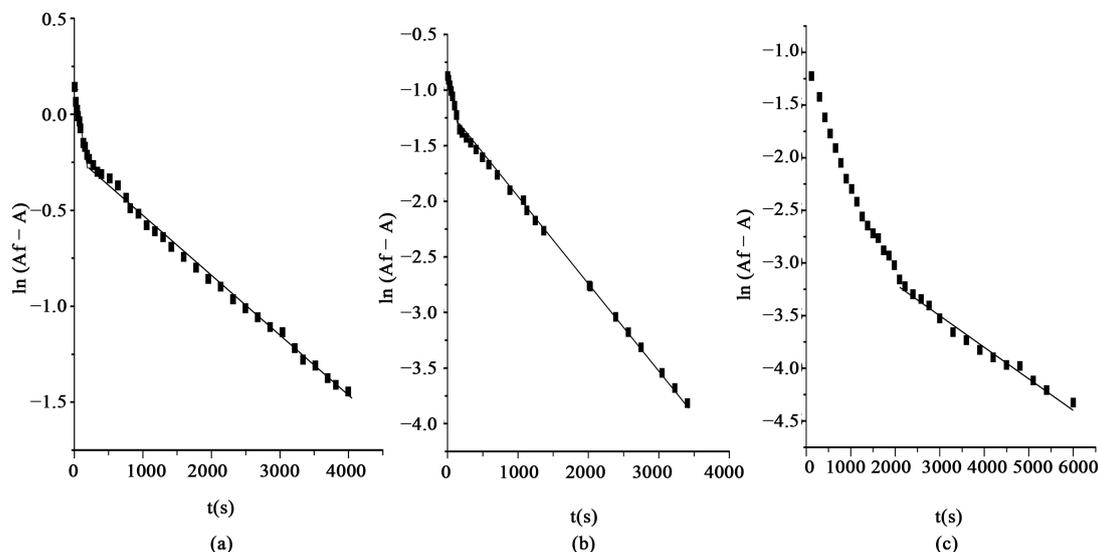


Figure 2. Graph $\ln(A_f - A)$ versus time (s) for the kinetics of the reaction of $\text{H}[\text{Ru}(\text{III})\text{Cl}_2(\text{H}_2\text{EDTA})]$ ($1.56 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) with AEATS; $[\text{AEATS}] = 0.35$ (a); 0.50 (b); and $0.20 \text{ mol} \cdot \text{dm}^{-3}$ in ethanol (c) ($\mu = 0.50 \text{ mol} \cdot \text{dm}^{-3}$ in NaCF_3COO , 298.15 K).

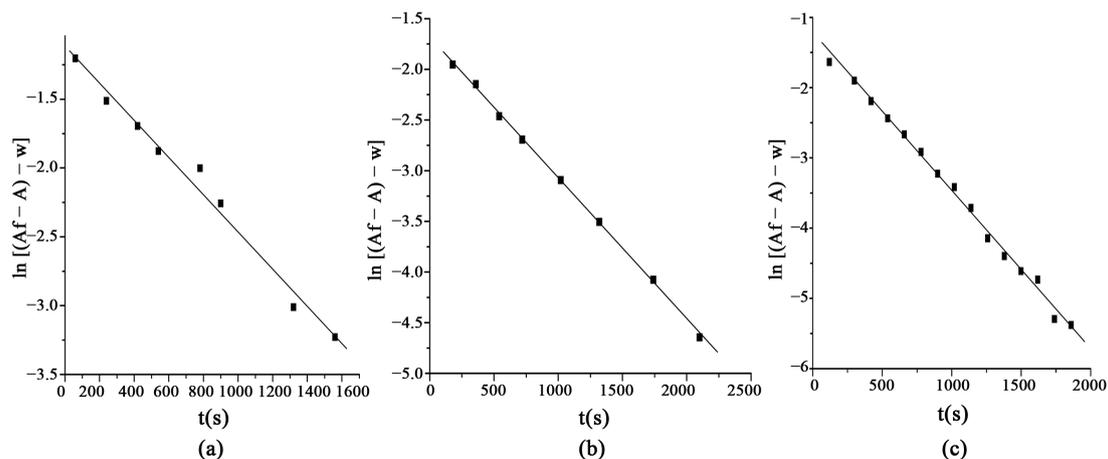


Figure 3. Graph $\ln[(A_f - A) - w]$ versus time (s) for the kinetics of the reaction $\text{H}[\text{Ru}(\text{III})\text{Cl}_2(\text{H}_2\text{EDTA})]$ ($1.56 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) with AEATS; $[\text{AEATS}] = 0.35$ (a); 0.50 (b); and $0.20 \text{ mol} \cdot \text{dm}^{-3}$ in ethanol (c) ($\mu = 0.50 \text{ mol} \cdot \text{dm}^{-3}$ in NaCF_3COO , 298.15 K).

Table 1. Kinetic data obtained for the formation of $\text{H}[\text{Ru}(\text{III})\text{Cl}_2(\text{H}_2\text{EDTA})]$ ($1.56 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) with the AEATS; $[\text{AEATS}] = 0.35$; 0.50 and $0.20 \text{ mol} \cdot \text{dm}^{-3}$ (ethanol) ($\mu = 0.50 \text{ mol} \cdot \text{dm}^{-3}$ in NaCF_3COO , 298.15 K).

$[\text{AEATS}]$ $\text{mol} \cdot \text{dm}^{-3}$	$\varepsilon_0 \times 10^{-2}$ $\text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$	$\varepsilon_1 \times 10^{-3}$ $\text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$	$\varepsilon_2 \times 10^{-3}$ $\text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$	$k_{\text{1obs}} \times 10^{+4} \text{ s}^{-1}$	$k_{\text{2obs}} \times 10^{+6} \text{ s}^{-1}$
0.35	1.7	4.4	9.4	13.5 ± 0.7	44.7 ± 0.3
0.50	2.9	2.4	4.4	14.2 ± 0.3	76 ± 1
0.20 (ethanol)	2.9	2.4	2.9	22.3 ± 0.4	460 ± 7

material (ε_0) are also shown in **Table 1** and with these data it was possible to confirm the experimental kinetic data (**Figure 4**). Observing the values of the molar absorptivity the following ion complexes may have formed

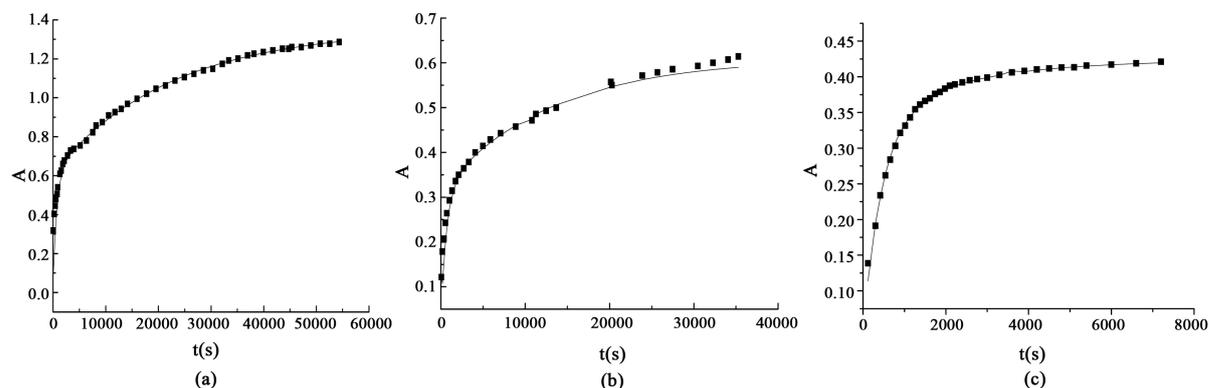


Figure 4. Kinetics of the reaction $\text{H}[\text{Ru}(\text{III})\text{Cl}_2(\text{H}_2\text{EDTA})]$ ($1.56 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$) with AEATS; $[\text{AEATS}] = 0.35$ (a); 0.50 (b); and $0.20 \text{ mol}\cdot\text{dm}^{-3}$ in ethanol (c) ($\mu = 0.50 \text{ mol}\cdot\text{dm}^{-3}$ in NaCF_3COO , 298.15 K). (■) Experimental data and (—) data using the values of Table 1, for the graphic treatment (Figure 2 and Figure 3) for successive reactions.

in this preliminary study of reactivity:

-ion complex with coordination number six, EDTA attached to the four positions, therefore, with two free carboxylate and the fifth and sixth ethylenediamine bound bidentate ($[\text{Ru}(\text{III})\text{en}(\text{EDTA})]^{1-}$, $\varepsilon = 9.4 \times 10^{+3} \text{ cm}^{-1}\cdot\text{mol}^{-1}\cdot\text{dm}^3$);

-ion complex with coordination number six, EDTA attached to the four positions, therefore, with two free carboxylate, one molecule of H_2O in the fifth and sixth ethylenediamine bound monodentate by NH_2 ($[\text{Ru}(\text{III})\text{-(EDTA)en}(\text{H}_2\text{O})]^{1-}$, $\varepsilon = 2.4 \times 10^{+3} \text{ cm}^{-1}\cdot\text{mol}^{-1}\cdot\text{dm}^3$) or by NH ($\varepsilon = 4.4 \times 10^{+3} \text{ cm}^{-1}\cdot\text{mol}^{-1}\cdot\text{dm}^3$);

-ion complex with coordination number six, with EDTA attached by five positions and sixth ethylenediamine bound monodentate by NH_2 ($[\text{Ru}(\text{III})\text{en}(\text{EDTA})]^{1-}$, $\varepsilon = 1.7 \times 10^{+3} \text{ cm}^{-1}\cdot\text{mol}^{-1}\cdot\text{dm}^3$);

-ion complex with coordination number six, with EDTA attached by five positions and sixth ethylenediamine bound monodentate by NH_2 and having its electrostatic interaction with the NH_2^+ group with the COO^- of EDTA ($\varepsilon = 2.9 \times 10^{+3} \text{ cm}^{-1}\cdot\text{mol}^{-1}\cdot\text{dm}^3$).

The study of this complex system with coordination number of six, with EDTA attached by five positions and for the sixth chloride ($\text{H}[\text{Ru}(\text{III})\text{Cl}(\text{HEDTA})]$) will facilitate the understanding of the reactivity presented when the ratio of the concentrations of the ligand AEATS with the complex of the order of more than 1000 times in solution, in these conditions there is the possibility of bonded reverse reactions in the complex through NH and NH_2 ethylenediamine of the AEATS.

4. Conclusion

The complex generated in solution by the reaction of $\text{H}[\text{Ru}(\text{III})\text{Cl}_2(\text{H}_2\text{EDTA})]$ complex with the AEATS modifier agent was characterized by a spectrophotometric study. Through the spectrophotometric study it revealed a band at 457 nm , attributed to the charge transfer ligand-metal. It was also possible to determine the kinetic constants (k_{obs}) for the formation of complexes with the ethylenediamine of AEATS ligand bound monodentate and bidentate. This system showed very rich and complex chemistry, where depending on the concentration ratio of the AETS modifier agent with $\text{H}[\text{Ru}(\text{III})\text{Cl}_2(\text{H}_2\text{EDTA})]$ complex, disproportionation reaction with formation of binuclear involving the III and IV species occurs, as suggested by Baar and Anson [18].

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