# Evaluation of the aquation and characterization of *trans-* dichloro-bis(ethylenediamine) cobalt(III) chloride

Victoria Jordan*, Farah Maryam*, Rishab Nayak*, Regal Lige Jiang*

Department of Chemistry, Boston University, 590 Commonwealth Avenue, Boston, MA

Introduction

Coordination complexes have been studied extensively to learn more about the defining characteristics of transition metals.[1] Transition metals, such as cobalt, in their various oxidation states produce vivid, differing colors. Differing oxidation numbers also correlate to different number of coordinated ions in the complex. Further, isomers of the same complex produce different colors and react differently in water. Due to the nature of ligand exchange, aquation is the slowest process a coordination complex can undergo. This study investigates ligand exchange kinetics in *trans-* dichlorobis (ethylenediamine) cobalt(III) chloride (complex **I**). After the compound was synthesized and characterized, its aquation was studied using UV/Vis spectroscopy for 24 hours at 25℃. We expected the final product of aquation to be *trans*-diaquobis (ethylenediamine) cobalt(III) chloride. The rate and order of reaction were calculated and used to determine the mechanism of the aquation of complex **I**.
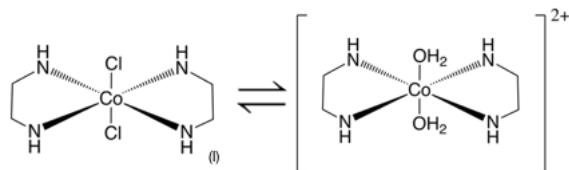
Figure 1: Expected reaction of *trans*-dichlorobis(ethylenediamine) cobalt(III) chloride (complex **I**) to form *trans*-diaquobis(ethylenediamine) cobalt(III) chloride.

Experimental

Synthesis of complex I.

$$2Co^{2+} + H_2O_2 + 2H^+ + 4en + 4Cl^- \rightarrow 2[Co(en)_2Cl_2]^+ + 2H_2O \quad (1)$$
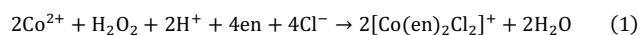
The synthesis equation of complex **I** is shown above (equation 1). A solution consisting of 4.00 g of cobalt(II) chloride hexahydrate and 32.00 mL of deionized water was placed on a magnetically stirring hot plate at 275℃. At two-minute intervals, 2.00 mL aliquots of 10% ethylenediamine totaling 16.00 mL was added to the solution and stirred for 10 minutes. Then, 1.25 mL of 30% hydrogen peroxide was added to the solution. After stirring for 15 minutes, 20.00 mL of 6 M hydrochloric acid was added, and the solution was brought to a boil.

The solution was left to evaporate for about 45 minutes, until about 10 mL remained. The solution was cooled to room temperature and green crystal formation was observed. Then, the crystals were filtered from solution and purified using chilled methanol.[2] The compound was subsequently dried at 100℃ in an oven until visibly dry, following which the dried crystals were completely reduced to a powder.

The percent yield was calculated to be 74.8%.

Characterization of complex I. IR spectroscopy was used to determine the types of bonds present and freezing point depression to validate its molar mass.

IR Spectroscopy. The IR spectrum of the synthesized compound was compared to its fingerprint pattern; a sharp absorption peak between 1430 cm^{-1} to 1620 cm^{-1}, representing the N-H bending mode of the ethylenediamine ligand was expected.[3] The N-H, C-H and Co-N stretching were also expected. The IR spectra of the synthesized compound is shown in figure 2.

Freezing Point Depression. The molecular weight of the complex was determined by dissolving approximately 0.80 g of complex **I** in 2.00 mL of dimethyl sulfoxide (DMSO). The freezing point of pure DMSO and DMSO-compound solution were measured. Rearranging the freezing point depression equation, it was possible to calculate the moles of complex **I** present, then the molecular weight. Calculations and equations are further shown in the supporting information.

Kinetics Analysis. Aquation was observed by recording the UV/Vis spectra of complex **I** in an excess of water over a 24-hour period at 25℃. By approximating that only one product was present at 24 hours, an equation was derived to determine the concentration of complex **I** from overlapping spectra of complexes **I** and **II** (equation 2). Due to the large excess of water present, no

change in the concentration of water was assumed, and pseudo first-order conditions were used to evaluate the rate order of the complex **I**. Then, the plot of the ln [complex **I**] versus time was used to determine the rate of the reaction of complex **I** to be first order.

$$[\text{complex I}] = (A(t) - A_{24}) \frac{[\text{initial}]}{A_o - A_{24}} \qquad (2)$$

Results and Discussion

The objective of the experiment was to synthesize and characterize *trans-* dichlorobis (ethylenediamine) cobalt(III) chloride (complex **I)** and evaluate the kinetics of its aquation. It was observed that the aquation of complex **I** at room temperature proceeded slowly to equilibrium in 24 hours. Rather than observing the expected product (figure 1), this study concluded that a *cis-* compound was produced.

The IR spectra of complex **I** (figure 2) confirms the properties of the expected complex. The N-H bending maxima occurs at 1579.67 cm^{-1}, consistent with the expected location of 1586 cm^{-1}.[3] The sharp N-H bending mode identifies the compound as the *trans-* isomer, as the *cis-* isomer would appear as a wide and relatively smooth absorption peak. In addition, the IR spectra indicates N-H stretching and C-H bending.[4] Ethylenediamine is volatile, therefore, any ethylenediamine detected is present in the complex as a ligand. IR also indicates a weak Co-N peak located at 480 cm^{-1}.[5]

Freezing point depression shows that the synthesized complex has a comparable molecular weight to the expected complex **I**. The average molecular weight of the synthesized compound from three trials was 287.41 g/mol, which was a 0.67% difference from the known molecular weight of the compound (285.49 g/mol, Sigma Aldrich).

To analyze the purity of the synthesized compound, the extinction coefficient of complex **I** was evaluated at 490 nm from the zero-hour absorption spectra (figure 3). Compared to a previous value of 14.1[6], the value of 17.8 differs by only 26.31%. This difference, in addition to the small percent difference in freezing point, suggests that slight impurities exist in the synthesized compound that have comparable freezing point properties and don't transmit light in the visible region.

While it was expected that the aquation of complex **I** would produce *trans*-diaquobis(ethylenediamine) cobalt(III) chloride (figure 1), the product observed did not match its UV/Vis characterization. The UV/Vis spectra of the reaction at 24 hours (figure 3) showed a large change in absorbance at 490 nm, indicating a significant change in product structure and extinction coefficient. This led the study to conclude the absence of the *trans-* isomer, and thus expected product.[6] Based on this and known kinetic properties, it was concluded that the observed product was *cis*-chloroaquobis(ethylenediamine) cobalt(III) chloride (complex **II**).
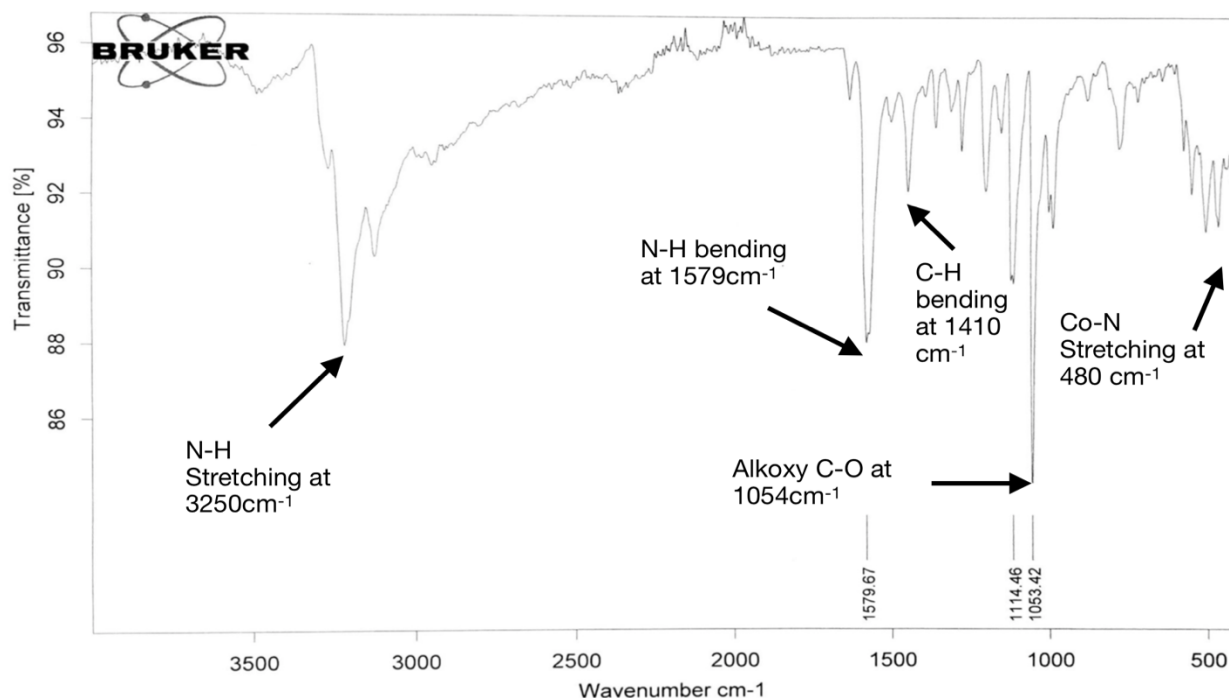

Figure 2: The infrared spectroscopy (IR) spectrum of complex **I**. A sharp N-H bending peak occurs at 1579.67 cm^{-1}; N-H stretching peak occurs at approximately 3250 cm^{-1}; alkoxy C-O occurs at 1054 cm^{-1}; C-H bending occurs at approximately 1410 cm^{-1}; and Co-N stretching at approximately 480 cm^{-1}. Based on the location and similarity of peaks, the synthesized compound was identified as *trans*-dichlorobis (ethylenediamine) cobalt(III) chloride (complex **I**).

The production of complex **II** is supported as the *cis*-isomer is more stable than the *trans*- isomer, thus the complex would reasonably have a tendency to isomerize from *trans* to *cis*. Further, the rate constant of the conversion of complex **I** to complex **II** is faster than the conversion of complex **I** to *trans*-diaquobis (ethylenediamine) cobalt(III) chloride due to increased steric hindrance.[7]

Of the spectra collected, the first isosbestic point at 444 nm remains constant through all 24 hours, and the other at 591 nm begins shifting after 10 hours indicating the slow formation of additional species (figure 3).

Further, on observing the reaction at 50°C, it can be seen that the order of the reaction is the same as at room temperature, indicating that the rate of the reaction is independent of temperature.

The aquation was visually characterized by a color change from green to red, and the half-life was marked by a grayish solution, similar to results reported by Pearson et. al., indicative of the same reaction to produce complex **II**. The consistency of the rate constant of the complete reaction 7.27×10^{-7} M^{-1} s^{-1} (equation 3) is supported by a calculated rate constant of 3.47×10^{-7} M^{-1} s^{-1} based on the half-life calculations shown in the supporting information.
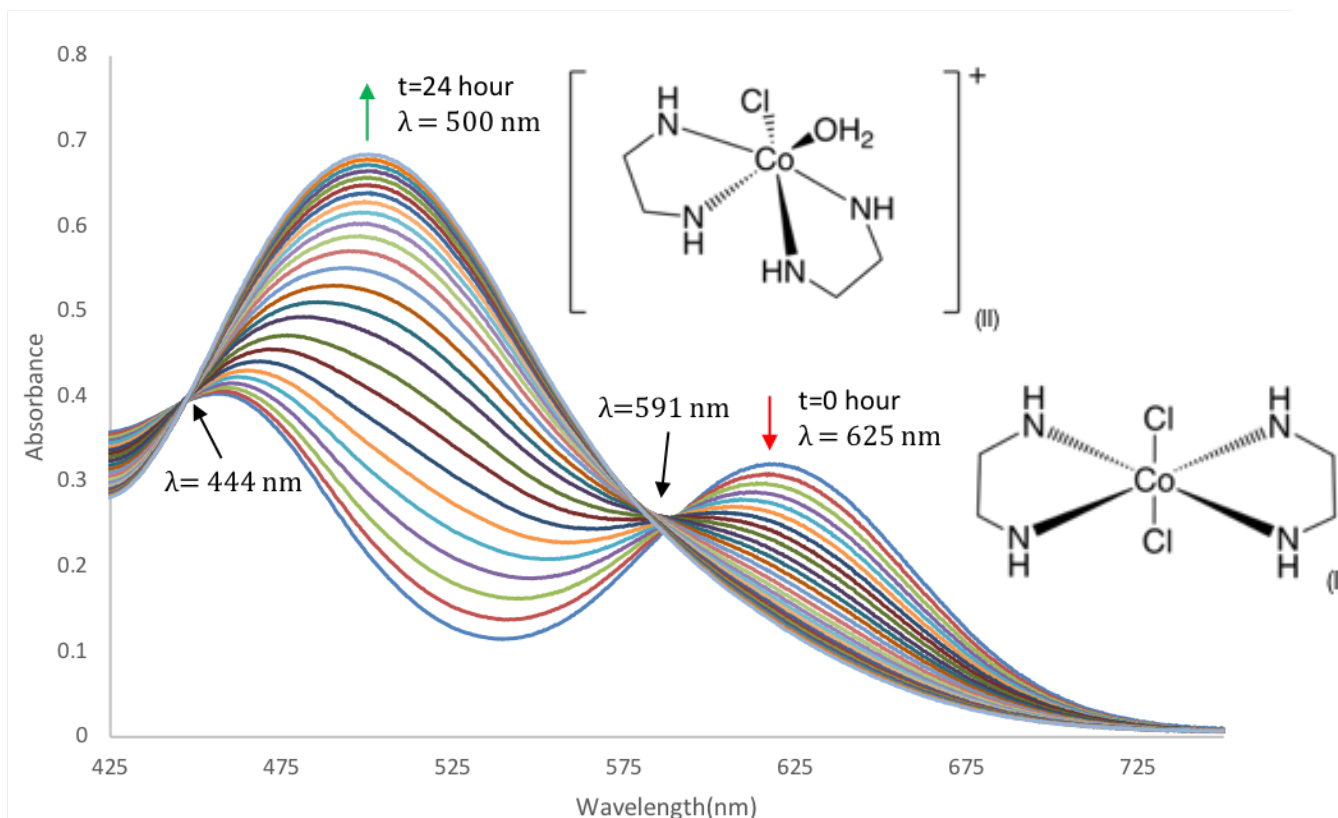

Figure 3: UV-vis spectra of the reaction of complex **I** in water at room temperature every hour over 24 hours to form complex **II**. Isosbestic points are indicated by black arrows at 444 nm and 591 nm. The increasing presence of complex **II** is indicated by a green arrow at the λ_{max} of 500 nm. The decreasing presence of complex **I** is indicated by a red arrow at an identifying peak at 625 nm; the λ_{max} was obstructed by the peak of complex **II** and not used to identify complex **I**.

Data from hours 21-24 were removed from the analysis of the rate (figure 4) because the reaction slowed down as it reached completion. Plotting the rest of the data led us to conclude that the reaction (figure 5) was first order in complex **I**; and the determination of complex **II** as the product indicated that the reaction was also first order in water. The pseudo rate constant calculated was 4.036×10^{-5} s^{-1} (figure 2), and accounting for the first order participation of water, the final rate constant was calculated to be 7.27×10^{-7} M^{-1} s^{-1}. The following second order rate equation was determined (equation 3).

$$\text{Rate} = 7.27 \times 10^{-7} \text{ M}^{-1}\text{s}^{-1}[\text{H}_2\text{O}][\text{complex I}] \quad (3)$$
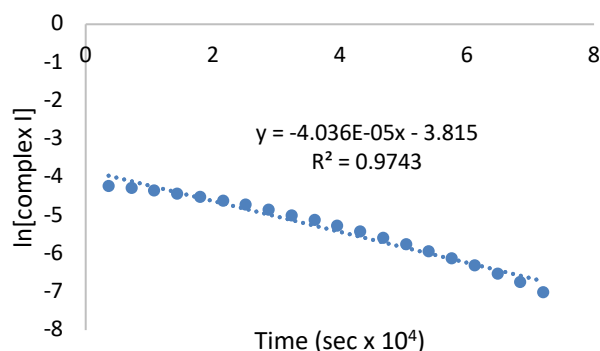
Figure 4: Plot of calculated ln [complex I] at each hour as determined from spectra at 500 nm. Based on the line of best fit, the rate order is determined to be first order, and k' is 4.036×10^{-5} s^{-1}. The deviations from linearity are assumed to be the result of the increasing presence of other species that were not corrected for in the determination for the absorbance of complex I. Data from hours 21-24 has been removed.

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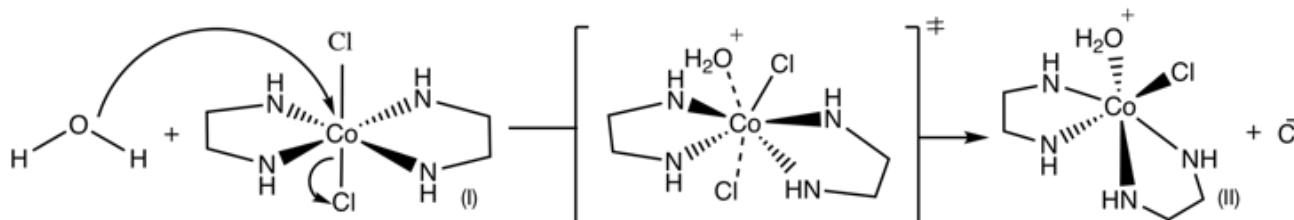
Figure 5: The associative ligand substitution between complex **I** and water to produce complex **II**. Complex **I** undergoes a backside attack by a water ligand. The transition state is marked by a seven-coordinate system with the bond weakening between complex **I** and a chloride and strengthening between complex **I** and water. The final product, complex **II**, is again a six-coordinate system with an inversion of configuration of the ethylenediamine ligands to yield the *cis* isomer.

Based on the determination of the product, reaction rate, and previous studies[7], the aquation reaction follows an associative ligand substitution mechanism. The water ligand acts as a nucleophile, initiating a backside attack on complex **I**. This leads to a seven-coordinate complex transition state. The final product, complex **II**, is the *cis*-isomer, due to inversion of configuration of the ethylenediamine ligands, with a water ligand in place of a chloride ligand. This mechanism is most likely to occur because the *cis*- isomer of this cobalt complex is more stable.

Conclusion

This study set out to synthesize and characterize *trans*-dichlorobis (ethylenediamine) cobalt(III) chloride (complex **I**) and measure the kinetics of its aquation. While it was predicted that the aquation of complex **I** would form an aquated *trans*- complex with the inner sphere chlorides replaced with water (figure 1), the reaction was found to be more elaborate in nature. Based on spectral and kinetic properties observed by this study and previous studies, the reaction of complex **I** in an excess of water was concluded to produce *cis*-dichlorobis (ethylenediamine) cobalt(III) chloride (complex **II**) through an associative ligand substitution mechanism (figure 5). Shifts in isosbestic points in spectral data (figure 3) indicate the increasing presence of other species this study was unable to identify. Further studies could work towards isolating these additional species and to characterize the mechanism of their formation. Continued studies can also work on studying the reaction in different solvents to further determine the role of water in the reaction.

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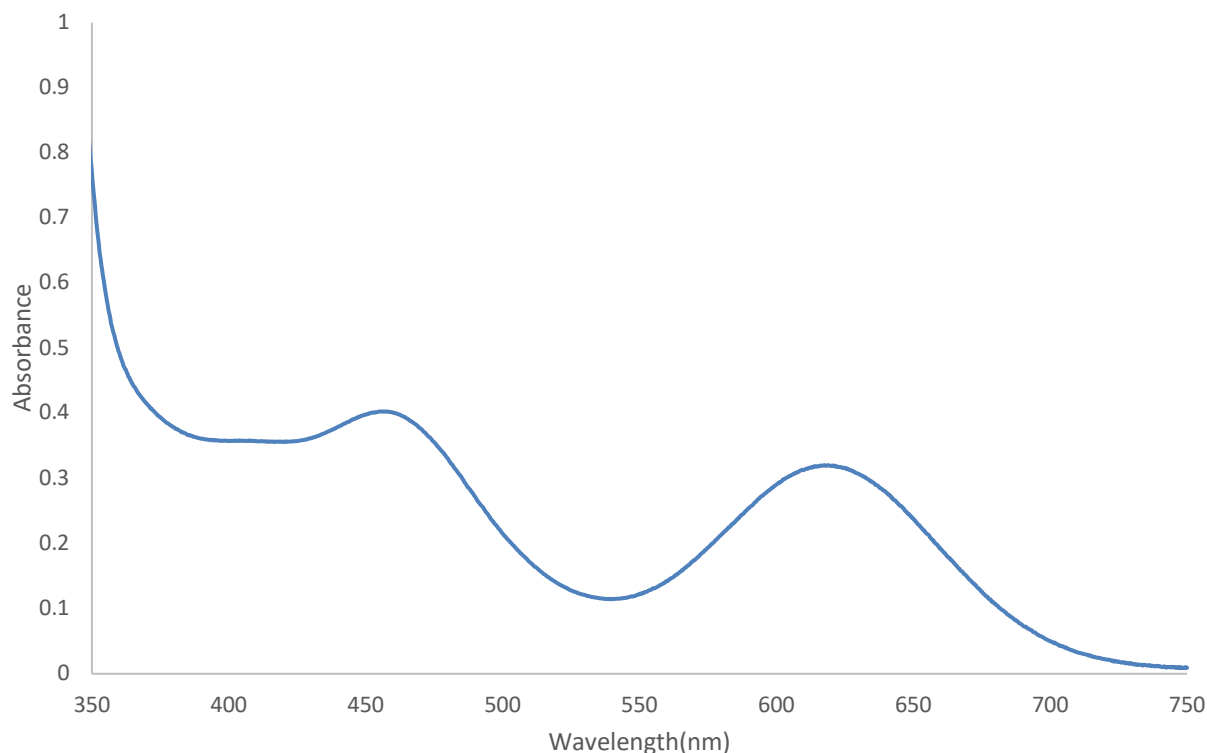
Figure 1: The UV-vis spectra of 0.10 M of complex **I** in water at time zero. The molar absorptivity value at 490 nm indicates the compound had a 26% difference from that of previous studies[2].

The deviation of the epsilon values at 490 nm of complex **I** from the expected value can be explained by the impurities present in the final product synthesized. The percent difference between the expected epsilon[2] and observed epsilon values are as shown –

$$\left(\frac{\epsilon_{experimental} - \epsilon_{actual}}{\epsilon_{actual}}\right)100\% = \left(\frac{17.81 - 14.1}{14.1}\right)100\% = 26.31\%$$

Percent Yield

To complete percent yield calculations, it was first determined that ethylenediamine (en) was the limiting reagent in the reaction.

$$2Co^{2+} + H_2O_2 + 2H^+ + 4en + 4Cl^- \rightarrow 2[Co(en)_2Cl_2]^+ + 2H_2O \quad (1)$$
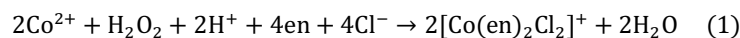
Next, it was determined how many moles of en were expected to be consumed in the reaction

$$\text{expected mol en} = \frac{(\% \text{ en solution})(\text{volume en solution added})(\text{density en})}{\text{molar mass en}} \quad (2)$$

$$\text{expected mol en} = \frac{(0.10 \text{ en solution})(16.00 \text{ mL en added})(0.8991 \text{ g mL}^{-1})}{60.2172 \text{ g mol}^{-1}} = 0.02389 \text{ mol}$$

Given a 2:1 ratio for moles of en consumed for complex **I** formed, the expected mass of complex **I** can be calculated.

$$\text{expected mass complex I} = (\text{mol en formed})\left(\frac{2 \text{ mol complex I}}{4 \text{ mol en}}\right)(\text{molar mass complex I}) \quad (3)$$

$$\text{expected mass complex I} = (0.02389 \text{ mol en})\left(\frac{2 \text{ mol complex I}}{4 \text{ mol en}}\right)(285.49 \text{ g mol}^{-1}) = 3.4101 \text{ g}$$

The result of equation 3 was used to determine the percent yield of the complex synthesized.

$$\text{percent yield} = \left(\frac{\text{mass complex synthesized}}{\text{expected mass of complex I}}\right) \times 100\% \quad (4)$$

$$\text{percent yield} = \left(\frac{2.5498\text{ g}}{3.4101\text{ g}}\right) \times 100\% = 74.8\%$$

Freezing Point

Sample calculation for trial 1:

$$\text{mol complex} = \frac{(\text{kg DMSO})\Delta T_f}{k_f} \quad (5)$$

$$\text{mol complex} = \frac{(2.00\text{ mL DMSO})\left(1.10\frac{\text{g}}{\text{mL}}\text{ DMSO}\right)\left(\frac{1\text{ kg}}{1000\text{ g}}\right)(19.3°\text{C} - 14.3°\text{C})}{4.07\frac{\text{kg}°\text{C}}{\text{mol}}} = 0.002703\text{ mol}$$

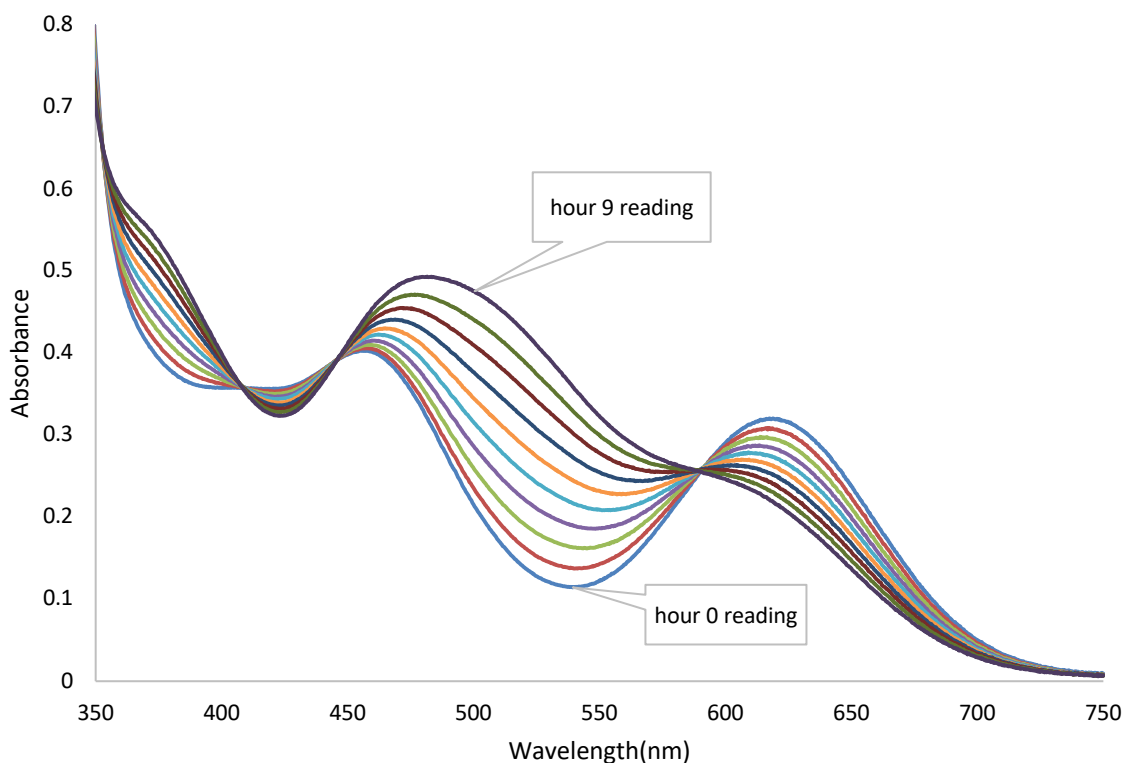$$\text{molar mass complex} = \frac{\text{mass complex used}}{\text{mol complex calculated}} \quad (6)$$

$$\text{molar mass complex} = \frac{0.7716\text{ g}}{0.002703\text{ mol}} = 285.48\text{ g mol}^{-1}$$

Percent Difference in Molar Mass

$$\% \text{ difference} = \left|\frac{x_0 - \mu_0}{\mu_0}\right| \times 100\% \quad (7)$$

$$\% \text{ difference} = \left|\frac{285.5 - 287.4}{287.4}\right| \times 100\% = 0.67\%$$

Figure 2: The UV-vis spectra of the reaction of complex **I** in water at room temperature every hour over 9 hours. The isosbestic points at 448 nm, 403 nm, and 590 nm indicate that among the possible products, one is being produced at a higher concentration and influences the absorbance more than the other species.

The derivation for the equation used to determine the concentration of trans-dichlorobis (ethylenediamine) cobalt(III) chloride at each point in time. At $\lambda = 500.4$ nm and 1 cm pathlength.

Henceforth, x represents $\text{trans} - [Co(en)_2Cl_2]Cl$

y represents $\text{trans} - [Co(en)_2Cl(OH_2)]Cl$

$$A_0 = A_x$$

$$A(t) = A_x + A_y$$

$$A(t) = \frac{A_o}{[\text{initial}]}[x] + \frac{A_9}{[\text{initial}]}[y]$$

$$A(t) = \frac{A_o}{[\text{initial}]}[x] + \frac{A_{24}}{[\text{initial}]}([\text{initial}] - [x])$$

$$A(t) = \frac{A_o - A_{24}}{[\text{initial}]}[x] + A_9$$

$$[x] = (A(t) - A_{24})\frac{[\text{initial}]}{A_o - A_{24}} \quad (7)$$

To determine the order of the reaction:

$$\text{Rate} = k[H_2O][x]^v$$

$$\text{Rate} = k'[x]^v$$

$$\text{Rate} = \frac{-d[x]}{dt} = k'[x]^0$$

$$\frac{-d[x]}{[x]^0} = k'dt$$

$$\int d[x] = \int -k'dt$$

$$x = -k't + x_0 \quad (8)$$

From the graph,

$$k' = 0.1453 \text{ hr}^{-1}$$

$$k' = 4.036 \times 10^{-5} \text{ } s^{-1}$$

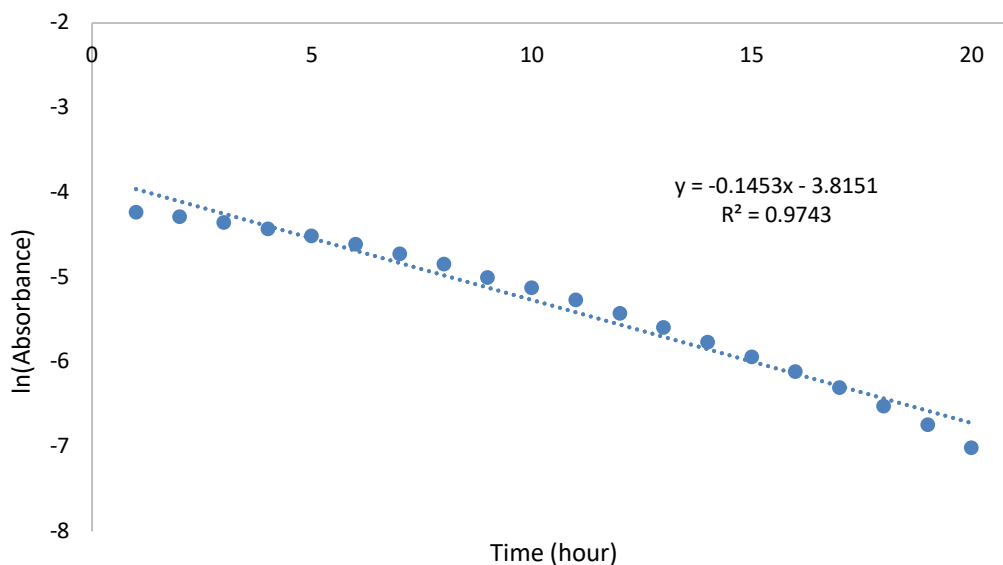**Determination of Rate Constant using Half Life[3]**

$$t_{1/2} = \left(\frac{1}{([B]_o - b[A]_o) * k}\right) * \ln\left(\frac{2[B]_o - b[A]_o}{[B]_o}\right)$$

$$k = \frac{\ln\left(\frac{2[B]_o - b[A]_o}{[B]_o}\right)}{t_{1/2} * ([B]_o - b[A]_o)}$$

$$[A]_0 = [\text{complex I}]_o = 0.0151669 \text{ M}$$

$$[B]_0 = [H_2O]_o = 55.5 \text{ M}$$

$$k = \frac{\ln\left(\frac{2 * 55.5M - 1 * 0.0151669 \text{ M}}{55.5 \text{ M}}\right)}{36000 \text{ s} * (55.5 \text{ M} - 1 * 0.0151669 \text{ M})} = 3.469 \times 10^{-7} \text{ M}^{-1}s^{-1}$$

Figure 3: Plot of the natural log of the approximate absorbances of complex **I** at each hour. Based on the line of best fit, the rate order is determined to be first order, and k′ is 4.036 × 10⁻⁵ s⁻¹. The deviations from linearity are assumed to be the result of the increasing presence of other species that were not corrected for in the determination for the absorbance of complex **I**. Data points from hours 21-24 have been removed, because the reaction had reached equilibrium and slowed.

$$k' = k[\text{H}_2\text{O}] \quad (9)$$

$$k = 7.27 \times 10^{-7} \text{ M}^{-1}\text{s}^{-1}$$

Therefore, the following second order rate equation was determined.

$$\text{Rate} = 7.27 \times 10^{-7} \text{ M}^{-1}\text{s}^{-1}[\text{H}_2\text{O}][trans\text{-dichloro-}] \quad (10)$$
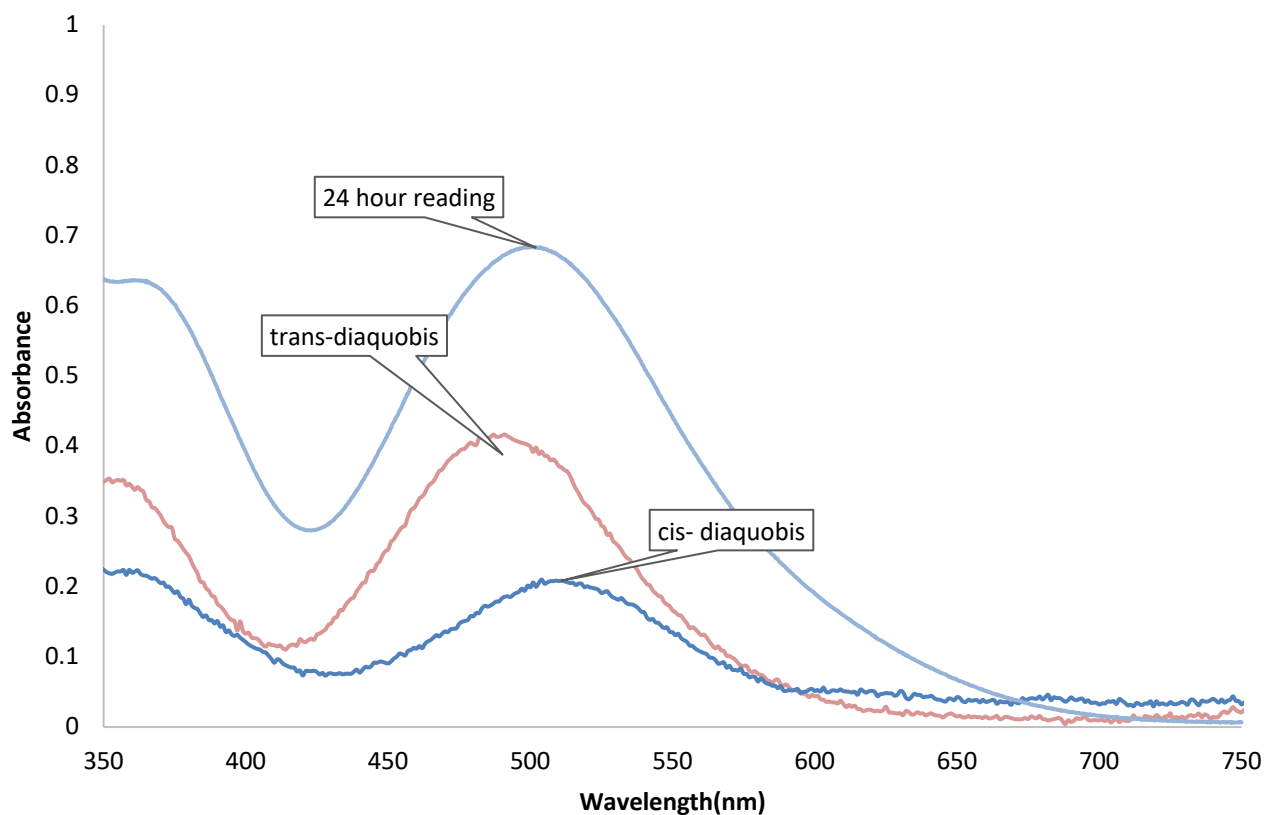

Figure 4: The UV/vis absorption spectra of other possible species produced by the aquation of complex **I**. Solutions were produced by driving halides off of the complex using an excess of silver nitrate solution. The spectra of neither solution have a peak that matches the product formed, making it impossible to identify the product based on the solutions spectra alone.
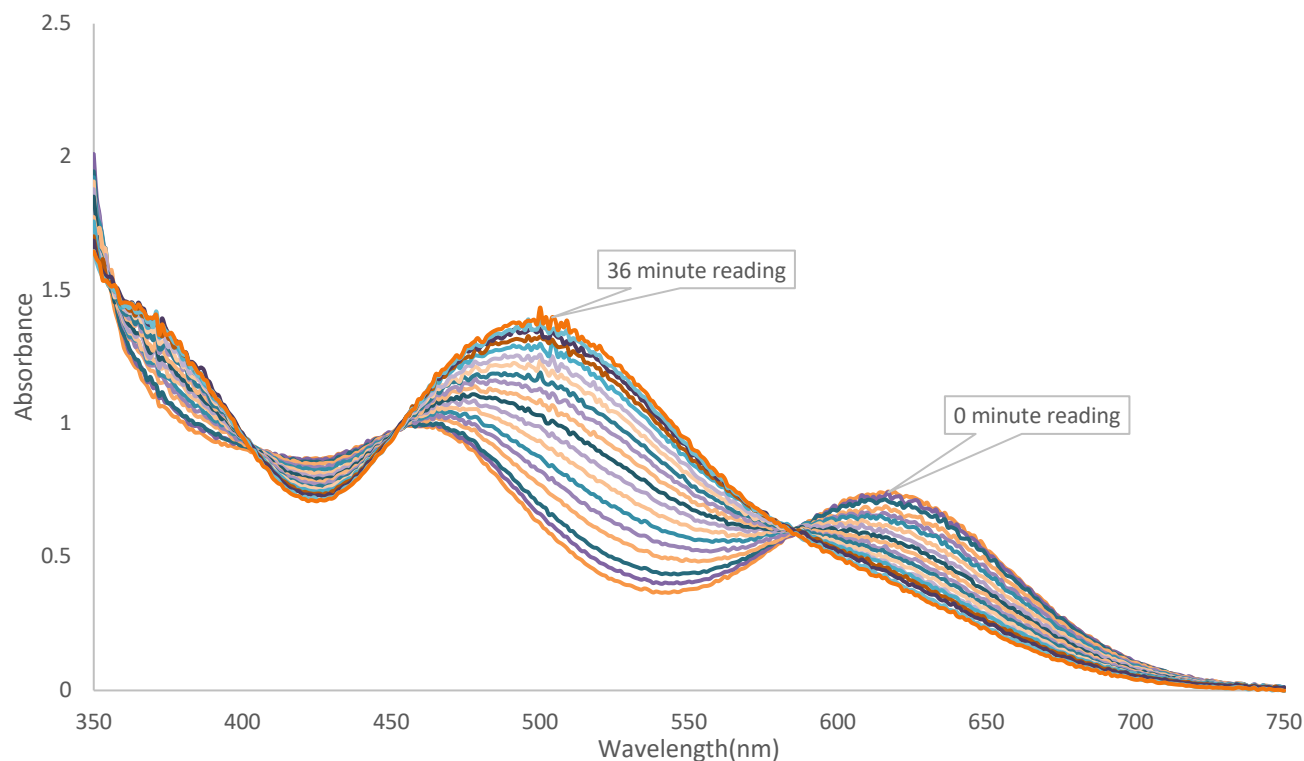
Figure 5: The UV/vis absorption spectra of the reaction of complex **I** in an excess of water at 50℃ to produce complex **II** recorded every 2 minutes. The reaction was measured using a fiber optic cable probe which caused the static readings. The spectral transition looks the same as at room temperature indicating heat doesn't change the nature of the reaction.

$$y = -1.175E\text{-}03x - 3.919$$
$$R^2 = 9.602E\text{-}01$$
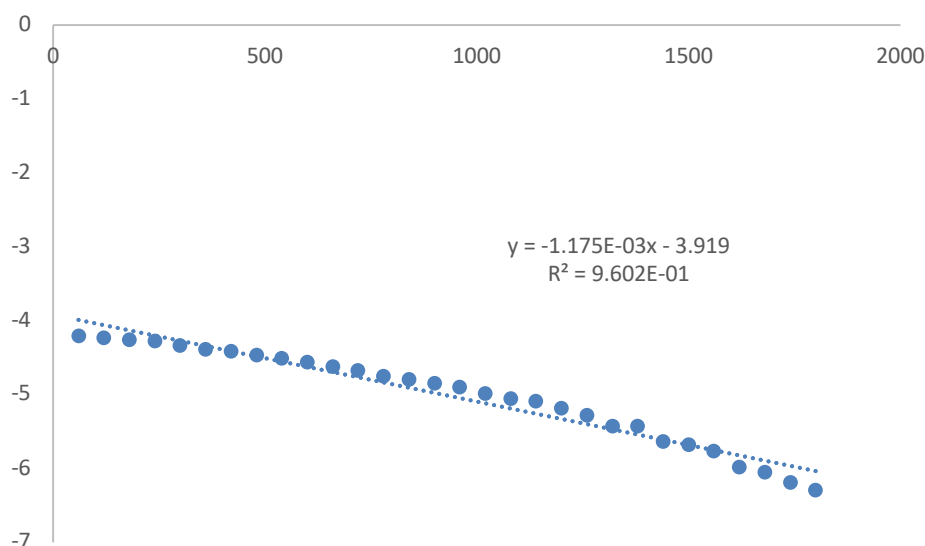
Figure 6: Plot of the natural log of the approximate concentration of complex **I** at each hour as determined from spectra at 500 nm where the presence of complex **II** increases for the reaction at 50℃. Based on the line of best fit, the rate order is determined to be first order, and k' is 1.175×10^{-3} s^{-1}. The deviations from linearity are assumed to be the result of the increasing presence of other species that were not corrected for in the determination for the absorbance of complex **I**. Data from hours 21-24 removed.

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