<u>Title:</u> Kinetics of Aquation of Pentaamminechlorocobalt(III) and Kinetics of Decomposition of Tetraamminecarbonatocobalt(III) Revisited. Synthesis, characterization, and determination of pK_a of coordinated water in aquopentaamminecobalt(III) trichloride

By

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Abstract:

The hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ in acidic solution follows a pseudo-first-order rate law, $rate = k'[A]^m$, in which k'=k[H₂O]ⁿ and A = $[Co(NH_3)_5Cl]^{2+}$. The order m was found by the method of initial rates to be ~1. The observed rate constant found at 25°C, 4.17×10^{-5} s⁻¹, was able to be compared to the literature value⁷ of 1.72×10^{-6} s⁻¹. This inconsistency is attributed to differences in ionic strength. The activation energy, E_a, was found to be 45 kJ/mol and the frequency factor, A, was found to be 3.8×10^3 s⁻¹. An enthalpy, Δ H, of 94 kJ/mol matched appropriately with the accepted value of 93 kJ/mol. Additionally, the pK_a of coordinated water in $[Co(NH_3)_5(H_2O)]Cl_3$ could be determined using titration and spectroscopy. The titrimetric method yielded a pK_a of 5.66, while the two spectroscopic methods gave pK_a's of 5.96 and 5.77. An average pK_a of 5.80 was determined, making the coordinated water ~10 billion times more acidic than uncoordinated water. Lastly, the kinetics of the decomposition of $[Co(NH_3)_4(CO_3)]NO_3$ were studied. The reaction follows a rate law *rate* = $k'[(NH_3)_4CoCO_3^+]^m$, where k' = [H⁺]ⁿ at a constant pH. The reaction was studied at three different pH's and the k' value determined for each. It was concluded that both m and n equal one, giving the reaction a second order rate law.

Introduction:

Coordination compounds are found in many biological processes. Perhaps the most widely known of these complexes are the heme molecules found in the hemoglobin of red blood cells. Each heme group has an iron(II) center that is able to reversibly bind oxygen, allowing for oxygen exchange throughout the body. Because of this and many other examples, studying such compounds and their chemistry is very important. This project aims to look at some of the basic principles of coordination chemistry in Co(III) complexes.

The first portion of this project deals with the kinetics of the hydrolysis of $[Co(NH_3)_5Cl]Cl_2$ (eq. 1)¹.



The reaction follows a pseudo-first-order rate law, $rate = k'[A]^m$, where $k' = [H_2O]^n$ and $A = [Co(NH_3)_5Cl]^{2+}$, because water is in excess. A calibration curve was first made from a Beer's law plot to ensure that the compounds' concentration can be determined from the absorbance at a wavelength, in this case, of 550 nm.

Secondly, the kinetics of decomposition of Carbonatotetraamminecobalt(III) (eq. 3) were studied using the UV/Vis spectrophotometer.



This reaction follows a pseudo-first-order rate law of $rate = k'[(NH_3)_4 CoCO_3^+]^m$, at a constant pH, where k' = $[H^+]^n$. The overall order of the reaction can be determined by finding the value of k' using the integrated rate law at varying H⁺ concentrations.

The last portion provides three methods to determine the acid dissociation constant (pK_a) of the coordinated water in $[Co(NH_3)_5(H_2O)]^{3+}$. Using a titrimetric method and two spectroscopic methods, the addition of base to the compound in aqueous solution (eq. 2) allows us to see how much more acidic the coordinated water is than uncoordinated water.



Experimental Section:

Instrumentation: Ultraviolet – Visible spectra were recorded using Genesys 10S UV-VIS Spectrophotometer (Model 610S serial number 2L5P123002)

Synthesis.

Recrystallization of [Co(NH₃)₅Cl]Cl₂: A crude sample of [Co(NH₃)₅Cl]Cl₂ was prepared using the method described by Schlessinger and Henderson et al.^{2,3} and was recrystallized to yield a pure crystalline compound according to the following procedure: The compound was placed in a 100 mL beaker containing 20-30 mL of deionized water. This was then placed in a hot water bath, where it sat for approximately 15 minutes and was stirred occasionally. 2-3 drops of concentrated HCl was added to the solution, and another 15 minutes of stirring was carried out. Once most of the compound was dissolved, the solution was filtered via vacuum filtration and the filtrate was refrigerated overnight to allow crystallization. This filtrate was again filtered by vacuum filtration. The resulting crystals were allowed to dry in a desiccator overnight.

 $[Co(NH_3)_4(CO_3)]NO_3$ was made and recrystallized using the methods described by Schlessinger⁴.

$$\label{eq:constraint} \begin{split} & [\mathrm{Co}(\mathrm{NH}_3)_5(\mathrm{H}_2\mathrm{O})]\mathrm{Cl}_3 \text{ was prepared according to the methods described by Williams et al}^5. \\ & \underline{\mathrm{Kinetics \ of \ Hydrolysis \ of \ [Co}(\mathrm{NH}_3)_5\mathrm{Cl}]\mathrm{Cl}_2} : \end{split}$$

Calibration Curve: A calibration curve was made for the reactant by taking the absorbance at 550 nm of varying concentrations and making a Beer's law plot. The same was done for the product, obtained after heating varying concentrations of the reactant in a hot water bath for 40 min.

Method of Initial Rates: After heating a 100 mL volumetric flask of 0.10 M HNO_3 in a 60°C water bath, a massed sample of the compound was added and the flask was stoppered and shaken. 3 mL aliquots were taken every 8 minutes for 40 minutes. Each aliquot was immediately placed in ice for five minutes, then taken out and left to reach room temperature for another five minutes before the UV-Vis spectrum was taken. This process was done for initial reactant concentrations of 0.0100 M, 0.0080 M, and 0.0060 M.

Arrhenius Data: A 100 mL volumetric flask containing 0.10 M HNO₃ was heated in an 80°C water bath and a massed sample of the compound was added to yield a solution with an initial concentration of 0.120 M. 3 mL aliquots were taken every 5 minutes for a period of 33 minutes. Each were immediately placed in ice for five minutes, then taken out and left to reach room temperature for another five minutes before the UV-Vis spectra were taken. The same was done at a temperature of 100°C and 3 mL aliquots were taken every 2-3 minutes for 13 minutes.

Decomposition of [Co(NH₃)₄(CO₃)]NO₃

Kinetics: A 3×10^{-3} M solution of the compound was made in a cuvette with a potassiumbiphthalate buffer of pH=3. UV-Vis spectra were recorded every 3 minutes for 36 minutes. The cuvette was removed from the spectrophotometer between each recording to maintain room temperature.

The same was done in a hydrochloric acid and glycine buffer of pH=2. The spectra were recorded at 1 minute intervals for 12 minutes and again the cuvette was removed from the machine in between each recording.

To create conditions for pH=1.2, 2 mL of 0.064 M HNO₃ was placed in a cuvette and 0.8 mL of a 3×10^{-3} M aqueous solution of the compound was added. The absorbance was taken using the Milton Roy Spectronic (Model 601 serial number 3610114266) every 10 seconds for about 80 seconds.

Determination of pKa of Coordinated Water in [Co(NH3)5(H2O)]Cl3

Titrimetric Method: The titrimetric method was carried out using 25 mL 2.5 mM aqueous solution of $[Co(NH_3)_5(H_2O)]Cl_3$. 6.2 µL of NaOH (resulting in 0.25 mmol of the base in the solution) were added at a time. The pH was recorded after each addition using a Pasco PassPort apparatus and DataStudio software.

Spectroscopic Method: The spectroscopic method was performed similarly. NaOH was added 0.25 mmol at a time to 10 mL of 10^{-3} M aqueous solution of $[Co(NH_3)_5(H_2O)]Cl_3$. The pH and UV-Vis spectrum were taken after each addition.

Results and Discussion:

Kinetics of Hydrolysis of [Co(NH3)5Cl]Cl2:

Calibration Curve: Calibration curves were made by graphing absorbance (*A*) versus concentration (*c*) for both the reactant and the product. The slope of a line on such a plot yields the molar extinction coefficient (ϵ) according to equation 4, Beer's law, where the pathlength (*l*) is equal to 1 cm.

$$A_{\lambda} = \varepsilon_{\lambda} lc \tag{4}$$

Because the molar extinction coefficient is unique to each compound at a given wavelength (λ), this provides a way to confirm that one has the desired compound. Additionally, ϵ values were used in the kinetics portion to calculate the concentration of the reactant at a given absorbance.

The molar extinction coefficient for our reactant, $[Co(NH_3)_5Cl]^{2+}$, was found to be 40.4 cm⁻¹ M⁻¹ (Figure 1), which is comparable to the literature value of 47.5 cm⁻¹ M^{-1 6}. For our product, $[Co(NH_3)_5(H_2O)]^{3+}$, $\epsilon = 21.1$ cm⁻¹ M⁻¹ (Figure 2). This is nearly matching the literature value for this compound, 21.0 cm⁻¹ M^{-1 7}.



Figure 1: Beer's law plot of reactant. $\varepsilon = 40.4 \text{ cm}^{-1} M^{-1}$



Figure 2: Beer's law plot of product. $\varepsilon = 21.1 \text{ cm}^{-1} \text{ M}^{-1}$.

Method of Initial Rates: Measuring absorbance over the course of the hydrolysis reaction at three different initial concentrations allowed us to determine the order (*m*) of the reaction in respect to $[Co(NH_3)_5Cl]^{2+}$, as well as the k' at 60°C.

The initial rates (v_0) of each trial were determined by plotting concentration of the reactant, determined from absorbance at 550 nm, versus time (Figures 3-8). The slope of each graph is the negative initial rate.

To calculate the concentration of the reactant (C_R) at a given absorbance, equation 5 may be used.

$$C_R = \frac{A_{total} - \varepsilon_P C_{R,0}}{\varepsilon_R - \varepsilon_P} \tag{5}$$

(A_{total} is total absorbance; ε_P is the molar extinction coefficient of the product, and ε_R is the coefficient of the reactant; $C_{R,0}$ is the initial concentration of the reactant)



Figure 3: UV-Vis spectra taken over the course of the hydrolysis reaction with initial concentration of 0.0100 M



Figure 4: Concentration vs Time for initial concentration of 0.0100 M. Initial rate is 8×10⁻⁷ M/s.



Figure 5: UV-Vis spectra taken over the course of the hydrolysis reaction with initial concentration of 0.0080 M



Figure 6: Concentration vs Time for initial concentration of 0.0080 M. Initial rate is 6×10^{-7} M/s.



Figure 7: UV-Vis spectra taken over the course of the hydrolysis reaction with initial concentration of 0.0060 M



Figure 8: Concentration vs Time for initial concentration of 0.0060 M. Initial rate is 4×10⁻⁷ M/s

Using the initial rates obtained from the three trials, a graph of the natural log of the initial rate versus the natural log of the reactant concentration can be made, according to equation 6.

$$\ln v_0 = m \ln[A] + \ln k' \tag{6}$$

([A] is the concentration of the reactant)

This graph (Figure 9) gives a slope equal to the order of the reactant, and a y-intercept equal to the natural log of k'.



ln(v0) vs ln(concentration)

Figure 9: ln(v0) vs ln(concentration of reactant).

The order, *m*, is about to 1.4. From this, we can assume that the rate is first order in respect to the reactant, $[Co(NH_3)_5Cl]^{2+}$. In addition, k' at 60°C is equal to 0.0004.

Arrhenius Parameters: The Arrhenius equation (eq. 7) can be used to find the activation energy (E_a) and frequency factor (A) for this reaction. The trials done at 80°C and 100°C (Figures 10-11) provide us with two additional rate constants, k', which can be found using the first order integrated rate law (eq. 8) (see Figures 12-15).

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln A$$
(7)
(T is temperature in Kelvin and R is the gas constant)

 $\ln [A] = -kt + \ln [A]_0$ (8)

(*t* is time)



Figure 10: UV-Vis spectra taken over the course of the reaction at 80 $^{\circ}\!\mathrm{C}$



Figure 11: UV-Vis spectra taken over the course of the reaction at 100 °C.



Figure 12: Plot of first order integrated rate law at 60 °C. Again, the $k' = 0.0004 \text{ s}^{-1}$.



ln(concentration) vs Time

Figure 13: Plot of first order integrated rate law at 80 °C. $k' = 0.0007 \text{ s}^{-1}$.



Figure 15: Unadjusted 100 °C plot.

With the rate constants found at three different temperatures, the Arrhenius equation can be plotted (Figure 16), giving a slope equal to $-\frac{E_a}{R}$ and a y-intercept equal to the natural log of the frequency factor, *A*.



Figure 16: Arrhenius plot of data.

The E_a comes out to be 45 kJ/mol and the frequency factor is 3.8×10^3 s⁻¹. The graph has been extrapolated to show the data at 25°C, which enables us to compare the k' value to that of Lay⁸. Our k' value of 4.17×10^{-5} s⁻¹ differs significantly from the literature value of 1.72×10^{-6} s⁻¹. This discrepancy can be attributed to differences in ionic strength.

The enthalpy of this hydrolysis reaction can be found by graphing the natural log of the equilibrium constant, K_{eq} , versus the reciprocal temperature in Kelvin (Figure 17). Refer to equation 9, where ΔH is the enthalpy and ΔS is the entropy.

$$\ln K_{eq} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$
(9)

According to the resulting plot, the enthalpy for the reaction is 94 kJ/mol. This is nearly equal to the value given by Lay (93 kJ/mol).



Figure 17: Plot of lnK versus 1/T.

Decomposition of [Co(NH₃)₄(CO₃)]NO₃

Assuming a pseudo-first-order rate at a constant pH, the rate law for this decomposition can be presented as $rate = k'[Co(NH_3)_4(CO_3)^+]^m$, where k'=k[H⁺]ⁿ. Therefore, the k' can be found by graphing the first order integrated rate law (see equation 8). Each graph and their respective absorbance spectra can be seen below (Figures 18-22 and Table 1).



Figure 18: $ln(C_R)$ vs Time at pH=3



Figure 19: UV/Vis spectra for decomposition at pH=3



Figure 20: $ln(C_R)$ vs Time at pH=2



Figure 21: UV/Vis spectra for decomposition at pH=2



Figure 22: $ln(C_R)$ vs Time at pH=1.2

Absorbance	Time
0.162	20
0.148	30
0.137	40
0.131	50

Table 1: Absorbance data ($\lambda = 525$) obtained on Milton Roy Spectronic 601 at pH=1.2

Because each of these graphs yield a straight line, the order in respect to $Co(NH_3)_4(CO_3)^+$, m, is equal to 1. The results for k', obtained from the slope of each graph, are shown along with the literature values determined by Dasgupta and Harris⁹ (Table 2).

Obtained Values		Literature Values	
pH	k'	pH	k'
3	0.001	3.05	0.0013
2	0.011	2.0	0.0160
1.2	0.0718	1.0	0.1200
T-11.2			

Table 2

Any discrepancies between the obtained values and the literature values can likely be attributed to differences in ionic strength. No accepted value could be found at pH=1.2.

The values of k' can be used to determine the order in respect to H^+ concentration, n. When one compares the factor by which the k' changed with the factor by which the [H⁺] changed, the order can be determined (Table 3).



Table 3

Because the k' value changes by nearly the same factor as the H^+ concentration in each case, the order, n, is 1. The reaction, therefore, is second order overall.

The value of k' is suggested by Dasgupta and Harris to be represented by equation 10.

$$k' = k_1(H^+) + k_0 \tag{10}$$

Graphing k' values as a function of H^+ concentration will give the values of k_1 , as shown in Figure 23.



Figure 23: k' vs the concentration of H^+

The value for k_1 , represented by the slope, is 1.1 M⁻¹ sec⁻¹. This is comparable to the value given by Dasgupta and Harris, which was 1.5 M⁻¹ sec⁻¹.

Determination of pKa of Coordinated Water in [Co(NH3)5(H2O)]Cl3

Titrimetric Method: A titration curve (Figure 23) was made to show the change in pH as the volume of base was increased. At half of the equivalence point (indicated on the graph), the pH is equal to the pK_a . Therefore, the pK_a according to the titrimetric method is 5.66.



Figure 24: Plot of pH vs Volume.

Spectroscopic Methods: Two methods were used to find the pK_a using the UV-Vis spectra (Figure 24).



Figure 25: UV-Vis spectra taken after each addition of base to the solution.

Method 1: A rearrangement of the Henderson-Hasselbalch equation (eq. 10), adjusted to include absorbance, can be used to find the pK_a of the coordinated water. When graphed, this can be determined from the x-intercept¹⁰ (Figure 25).

$$Log\left[\frac{A_{HA}-A_{i}}{A_{i}-A_{A-}}\right] = pH_{i} - pK_{a}$$
(10)
In this case, the pK_a is 5.96.



Figure 26: x-intercept yields pK_a.

Method 2: The maximum wavelengths (λ_{max}) are taken from the spectrum with the highest pH and the one with the lowest pH. In this case, the highest pH was 6.96, which has a λ_{max} of 500 nm. The lowest pH was 5.21, with a λ_{max} of 495 nm. A plot of absorbance versus pH is made (Figure 27) and the series of absorbance at both wavelengths are graphed, resulting in two lines. The pH at which these two wavelengths have the same absorbance equals the pK_a. In Figure 23, the two points closest to the intersection on both lines were taken to give a clearer picture of where they intersect. The calculation is shown below:

0.0293x - 0.0400 = 0.0267x - 0.02500.00260x = 0.0150x = 5.77

Therefore, the pK_a of the coordinated water according to this method is 5.77.



Figure 27: The spectrum with the highest pH has a maximum wavelength of 500 nm, while the spectrum with the lowest pH, the reactant, has a maximum of 495 nm.



Figure 28: Absorbance vs pH at both 500 nm (solid line) and 495 nm (dotted line).



Figure 29: A closer look at the intersection of the two lines.

 pK_a of coordinated water: The three methods give an average pK_a of 5.80.

Method	pKa
Titrimetric	5.66
Spectroscopic #1	5.96
Spectroscopic #2	5.77
Average:	5.80

Uncoordinated water has a pK_a of 15.7. This makes the water molecule in $[Co(NH_3)_5(H_2O)]^{3+}$ ~10 billion times more acidic.



Conclusion:

A good deal of the findings here correspond with the proven literature values, save the instances where ionic strength was not maintained and where no accepted value was available (referring to the pK_a of coordinated water). The methods and compounds used, therefore, provide an appropriate starting point when studying coordination chemistry.

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