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Kinetics of the Reaction between Ni(tetren)$^{2+}$and Bipyridine

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In this paper is reported an unexpected reaction order and mechanism for the ligand exchange reaction between Ni(tetren)$^{2+}$ and the bidentate ligand, 2,2'-bipyridine. Kinetic studies were performed by the method of uv/visible spectrophotometry to follow product formation at 307 nm. Reaction conditions included aqueous solutions held at an ionic strength at 0.10 M and a temperature of 25.0 ^{0}C. Experiments were first performed to determine the order in Ni(tetren)$^{2+}$. These experiments were performed at constant pH under pseudo-order conditions with [bipy] in excess over [Ni(tetren)$^{2+}$] by at least a factor of 20. These studies show the reaction to be first-order in Ni(tetren)$^{2+}$. The order in bipy was then determined by varying [bipy] at constant [Ni(tetren)$^{2+}$] and constant pH, where results support an order in bipy of one. Last of all, varying the pH between 6 and 5 demonstrates that [H$^+$] accelerates the reaction rate, and shows that the order in [H$^+$] is one. Data from all three types of experiments support a rate law of the form: Rate = k [Ni(tetren^{2+})] [bipy] [H$^+$] with $k = 2.27 \times 10^6$ M^{-2}s^{-1} . This rate constant corresponds to the hydrogen ion assisted attack of bipy on Ni(tetren)$^{2+}$ This work is significant because it supports a mechanism that is a hybrid between associative and dissociative models in which a proton assisted pathway is dominant.

Keywords: Kinetics Coordination Chemistry

Introduction

Investigations into aqueous solution inorganic chemistry tend to center around metals that are attached to ligands, and this resulting class of molecules is known as coordination complexes, a field discovered by Alfred Werner. Such metal complexes have numerous applications in medicine. For example, the serendipitous discovery of the drug cisplatin by Barnett Rosenberg and Loretta Van Carr has had a profound impact on curing specific forms of cancer.[1] Moreover, such medicines aid the treatment of arthritis, diabetes, and hypertension[2], and are commonly used as chelating agents in treating metal intoxication, and as signaling agents for radioisotope identification of cancer[3].

Metal complexes have also been shown to have many properties that are extremely useful outside of direct medicinal uses. These compounds can be used in the separation of organic ligands which are becoming much more prevalent in modern organic chemistry[4,5,6]. In addition, chelating ligands such as tetren appear in the environment, and may affect mineral dissolution, and metal-mobilization.

In the laboratory, nickel complexes are often selected as model systems for study because they are well characterized, and are generally inert, which means that they react slowly enough to be followed by visible spectrophotometry. Hence the effects of bound ligands on rate constants are measurable, and the ligand association and dissociation reactions of Ni(II) are a continuing field of study[7,8,9,10,11,12,13].

The focus of this research project performed in undergraduate physical chemistry lab is a molecule called tetraethylenepentaminenickel(II) or Ni(tetren)$^{2+}$. Few studies have appeared on this compound [14]. The primary objective is to unravel the kinetics and mechanism of its ligand substitution reaction with 2,2'-biypridine (bipy). More specifically, one goal is to to determine whether the mechanism is associative or dissociative as shown below in (A) and (B) below where L_5 and L_2' represent tetren and bipy respectively:

(A) Associative Mechanism
i) $NiL_5 + L_2' \rightarrow L'\text{-}L'\text{-}NiL_5$
ii) $2L_2' + L'\text{-}L'\text{-}NiL_5 \rightarrow Ni(L_2')_3 + L_5$
or
(B) Dissociative Mechanism
i) $NiL_5 \rightarrow Ni + L_5$
ii) $Ni + 3L_2' \rightarrow Ni(L_2')_3$

In the associative mechanism, a ternary complex is formed in step (i). Such reactions are known to be fast, and are usually followed by stopped-flow methods[15]. Ternary complex reactions are generally described by the Eigen-Tamm Mechanism which is a rapid metal ion complexation reaction where the metal ion is desolvated as the rate limiting step in forming complexes with ligands. Hence, in the associative mechanism, fast ternary complex formation in (i) is followed by slow ligand exchange in step (ii). This investigation focuses on the slow ligand exchange reaction between bipy and Nitetren)$^{2+}$.

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Experimental

Reagents

The following high purity reagents were purchased from Sigma-Aldrich Corporation: nickel(II) nitrate hexahydrate (99.999%), tetraethylenepentamine pentahydrochloride (98%), 2,2'-bipyridine (> 99%), and 2-(N-morpholino)ethanesulfonic acid or MES (>99.5%). Doubly distilled water, passed through a Millipore Nanopure water purification system was used. Other reagents such as sodium cyanide were reagent grade. Bipy solutions are light sensitive and should be stored in the dark.

Safety

Workers should review all Material Safety Data Sheets and heed safety warnings. One special precaution is to avoid skin contact with 2,2'-bipyridine by wearing gloves. In addition, nickel(II) nitrate is a strong oxidizer, while tetren can evolve a flammable hydrogen gas when put in contact with metals. Hence, all chemicals must be stored and disposed of properly.

Most important of all, please note that life-threatening hazards are associated with using NaCN, and the described procedure for its use must be performed only by an experienced analyst using a fume hood, and with all cyanide solution pH values being maintained near 10 with standard ammonia/ammonium chloride buffer. Proper disposal of reagents is also a necessity. Additionally, NaCN must be stored in a locked safety cabinet when not in use.

Preparation and Standardization of Ni(tetren)$^{2+}$

The Ni(tetren)$^{2+}$ complex was prepared by mixing equal volumes of 0.10 M $Ni(NO_3)_2$ and 0.10 M tetren with a ratio of nickel to tetren at 1.05. The reaction was allowed to proceed for several hours while gradually raising the pH to about 11 using NaOH pellets. Excess nickel as the hydroxide was removed by vacuum filtration using a 0.2 micron Millipore filter, and the pH of the resulting complex was lowered to the range 6.5 to 7 for storage. The overall reaction for this preparation is:

$$Ni^{2+}(aq) + \text{tetren}(aq) \rightarrow \text{Ni(tetren)}^{2+}(aq) \tag{1}$$

The exact nickel complex concentration was determined by adding a 100-fold excess of sodium cyanide to an aliquot of Ni(tetren)$^{2+}$ to convert it to $Ni(CN)_4^{2-}$ at pH 10. The absorbance of this solution at 267 nm (ε = 1.13 x 10^4 $M^{-1}cm^{-1}$) was converted to concentration using the standard Beer-Lambert calibration curve, shown in Figure 1, that was generated from nickel(II) tetracyanide prepared from $Ni(NO_3)_2$ and excess NaCN at pH 10.

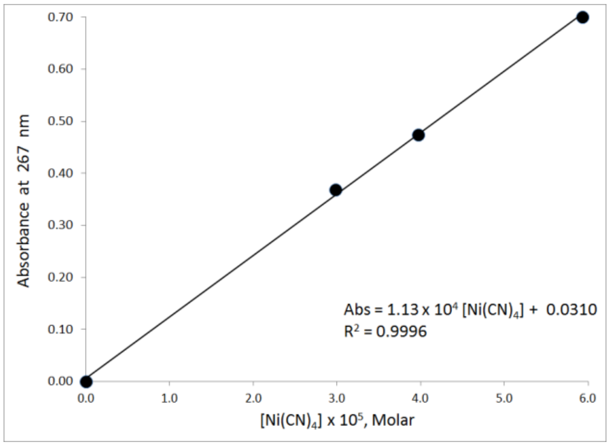

Figure 1: Calibration curve for the standardization of Ni(tetren)$^{2+}$.

Procedure for Kinetic Runs

All kinetic runs were monitored using an Agilent 8453 UV/Vis spectrophotometer with Peltier temperature control at 25°C ± 0.1°C in a quartz cell with 1 cm pathlength. An Oakton High Precision pH meter with Fisher Accumet glass and calomel reference electrodes was employed. Reactant solution pH was stabilized between 5.00 and 6.00 with the addition of MES buffer[12], and was adjusted to an exact value with dilute sodium hydroxide or hydrochloric acid. MES is ideally suited for this system because its pK_a is 6.09, and because it is noncomplexing. Sodium chloride was used to adjust the reaction solution ionic strength to 0.10 M. Kinetic runs were carried out in a 100 mL double jacketed beaker maintained at 25.0 ^{0}C using a Fisher Isotemp controller. Mixing was performed with magnetic stirring. High precision digital pipets introduced reagents into the reaction beaker. For each kinetic run, the following general experimental procedure was employed:

1. Calibrate the pH electrodes with pH 4 and 7 buffer solutions at 25.0 ^{0}C.
2. Warm up the Agilent 8453 spectrophotometer and zero it at 307 nm using a blank solution containing MES buffer and NaCl.

To the double jacketed reaction beaker on a magnetic stirrer, add the following reagents in order:

3. Add Type I water from a buret. The total solution volume will be 75.0 mL.
4. Pipet MES buffer solution to attain a concentration of 0.025 M (stock solution at 0.500 M).
5. Pipet NaCl solution to attain an ionic strength of 0.100 M (stock solution at 4.00 M).
6. Pipet bipyridine solution to attain a typical concentration of 4.00 x10^{-4} M (stock solution at 0.0140 M).
7. Adjust pH to the desired value using NaOH (only a few drops are required).
8. Let the system equilibrate to constant pH at 25.0 ^{0}C.

9. Initiate reaction by pipetting Ni(tetren)$^{2+}$ (stock solution at 6.70 x 10^{-4} M) into the system to attain a concentration of 1.00 x 10^{-5} M, and mix.
10. Remove a 3 mL sample, transfer to a cuvette, insert it into the spectrophotometer and start collecting absorbance vs time data.
11. Monitor solution pH.

The amount of NaCl needed to maintain ionic strength μ at 0.10 was computed from the equation:

$$\mu = 0.5\{\, [Na^+](-1)^2 + [Cl^-](-1)^2 + [A^-](-1)^2 + [H^+](+1)^2 + [Ni(tetren)^{2+}](+2)^2 \,\}$$

where [A$^-$] represents the anion form of MES, and where the concentrations of ions not shown are small and can be neglected.

Spectral Data

All reactions were run using pseudo-order conditions with the [bipy] to [Ni(tetren)$^{2+}$] ratio at least 20. Reaction mixture solutions were monitored by tracking reaction mixture absorbance at 307 nm. At this wavelength, although the spectra of reactants and products overlapped, it was still possible to compute [Ni(tetren)$^{2+}$] using the measured molar absorptivity values of reactants and products as listed in table 1.

Table 1. Molar absorptivity (ε) values of reactants and products at 307 nm and b = 1 cm.

Compound	Molar Absorptivity M^{-1} cm^{-1}
Ni(bipy)$_3$	ε_1 = 3.41 x 10^4
Hbipy$^+$	ε_2 =1.02 x 10^4
Bipy	ε_3 =475
Ni(tetren)$^{2+}$	ε_4 =17.8

Results

Proposed Model

The overall reaction is, in simplest terms, a substitution reaction involving the exchange of tetren bound to nickel with three bipyridine:

$$(3)\qquad Ni(tetren)^{2+} + 3bipy \rightarrow Ni(bipy)_3^{2+} + tetren$$

Data analysis is based on a proposed model for the reaction. If experimental data fits the model, then the model is deemed a success. Three assumptions define the proposed model:

Assumption 1: The reaction is first-order in [Ni(tetren)$^{2+}$].

Assumption 2: The reaction is first-order in [bipy].

Assumption 3: In the initial step of reaction, a ternary complex is not formed.

Using assumption 3, mass balanced equations are written for each species in the reaction mixture including Ni(bipy)$_3$, bipy, Hbipy$^+$, and Ni(tetren)$^{2+}$. These expressions are substituted into absorbance equations (4) and (5) below at time infinity and time t for any reaction mixture:

$$(4)\qquad A_\infty = b\,\{\varepsilon_1[Ni(bipy)_3]_\infty + \varepsilon_2[Hbipy^+]_\infty + \varepsilon_3[bipy]_\infty + \varepsilon_4[Ni(tetren)^{2+}]_\infty\,\}$$

$$(5)\qquad A_t = b\,\{\varepsilon_1[Ni(bipy)_3]_t + \varepsilon_2[Hbipy^+]_t + \varepsilon_3[bipy]_t + \varepsilon_4[Ni(tetren)^{2+}]_t\,\}.$$

In the above equations, the ε values correspond to each respective species, as listed in Table 1. Solving these equations gives the molar concentration of Ni(tetren)$^{2+}$ at any time t:

$$(6)\ [Ni(tetren^{2+})] = \frac{(A_\infty - A_t\ )}{b\,\{\,\varepsilon_{Ni(bipy)_3} - 3\varepsilon_{bipy} - 3\varepsilon_{Hbipy}\left(\frac{[H]^+}{K_a}\right)\}}$$

Equation (6) represents the proposed model for [Ni(tetren)$^{2+}$] for this system in which a ternary complex is presumed absent. In this equation, A$_\infty$ represents the reaction mixture absorbance at time infinity while A$_t$ represents reaction mixture absorbance at time t. In the denominator, b is the path length equal to 1 cm, and the ε's represent Molar absorptivity's of each respective species.

From equation (3), the rate of formation of Ni(bipy)$_3$ must be equal to the rate of disappearance of Ni(tetren)$^{2+}$. Additionally, assumptions 1 and 2, that the reaction is first-order each in [Ni(tetren)$^{2+}$] and [bipy] gives the following proposed rate law expression:

$$(7)\quad \frac{-d[Ni(tetren)^{2+}]}{dt} = k\ [\ Ni(tetren)^{2+}]\ [bipy\ ]$$

Under pseudo-order conditions in bipy, the above equation becomes:

$$(8)\qquad \frac{-d[Ni(tetren)^{2+}]}{dt} = k^0[\ Ni(tetren)^{2+}]$$

where k^0 is the pseudo-first order rate constant given by k^0 = k [bipy]. Integrating this expression gives the familiar first-order integrated expression:

$$(9)\quad log[Ni(tetren)^{2+}] = \log[Ni(tetren)^{2+}] + k^0t/2.303$$

Equation (9) represents the proposed model for this system, where [Ni(tetren)$^{2+}$] is computed from equation (6) using the assumption that no ternary complex is formed. For an actual kinetic run, at each time datum, [Ni(tetren)$^{2+}$] was computed by equation (6) in a Microsoft Excel spreadsheet.

Determination of Order in [Ni(tetren)$^{2+}$]

To determine the reaction order in [Ni(tetren)$^{2+}$], experiments were run at constant pH and constant [bipy] while following the change in reaction mixture absorbance at 307 nm over time.

Collected data generated absorbance versus time plots such as the one shown in Figure 2 where the increase in absorbance for a kinetic run at pH 5.31 is due to the formation of product Ni(bipy)$_3$.

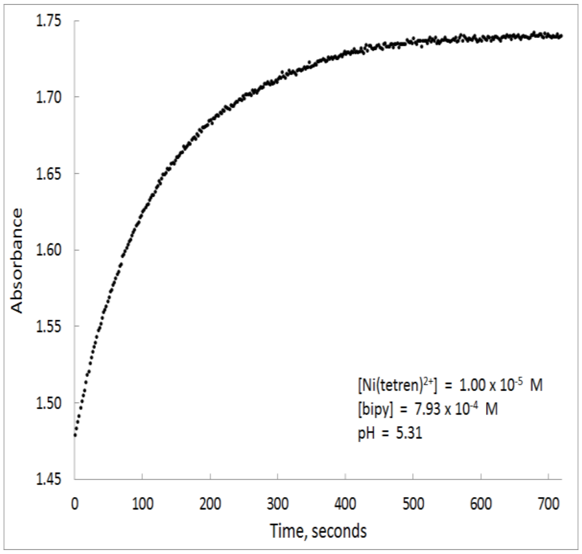

Figure 2: Increase in Absorbance (λ_{307}) from formation of Ni(bipy)$_3$ over time.

Using the data displayed in Figure 2, equation (6) allows computation of [Ni(tetren)$^{2+}$], and equation (9) provides log[Ni(tetren)$^{2+}$] values. An experimental plot of log[Ni(tetren)$^{2+}$] versus time t for this kinetic run, is shown in Figure 3 below, where the negative of equation (9) is plotted in order to produce a graph that is visually aesthetic. The plot in Figure 3 shows that equation (9) is obeyed because it is linear for more than two half-lives with an R^2 of 0.998. The pseudo first-order rate constant of $k^0 = 7.42 \times 10^{-3}\ s^{-1}$ is computed from 2.303 x slope. These results support assumption 1, that the rate law is first-order in [Ni(tetren)$^{2+}$].

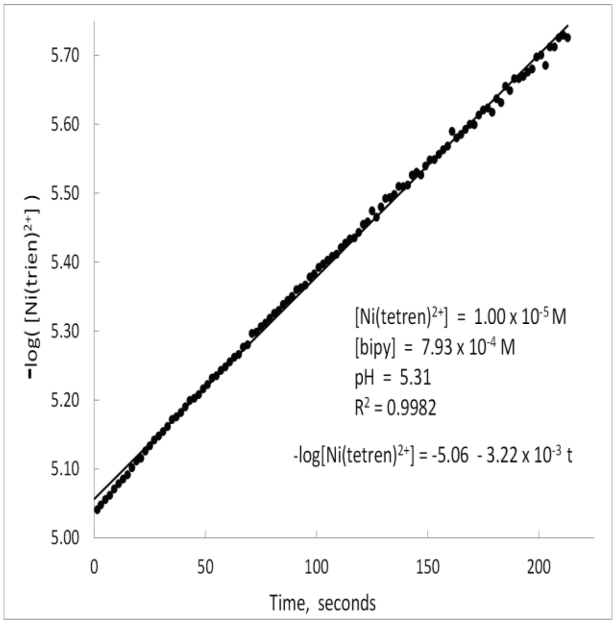

Figure 3: First-order behavior in Ni(tetren)$^{2+}$ as shown by a log[Ni(tetren)$^{2+}$] vs time plot.

Determination of Order in [bipy]

The next phase of data analysis involved determination of the reaction order in [bipy]. Experiments were run at constant [Ni(tetren)$^{2+}$] and constant pH while varying the bipy concentration. The data is summarized in Table 2 where each first-order rate constant value represents the average of triplicate runs or more, except for the run marked with an asterisk where duplicate runs were made. Standard deviations are reported in the table for each rate constant.

Determination of Order in [H$^+$]

Additionally, in order to determine the pH effect, pH was varied between 6.00 and 5.00 at constant Ni(tetren)$^{2+}$ and constant bipy, and this data is also compiled in Table 2. The lower limit pH was partly limited to 5.0 due to the high molar absorptivity of Hbipy$^+$.

Table 2: First-order rate constant data for the Ni(tetren)$^{2+}$- bipy reaction at 25.0 ^{0}C while varying [bipy] and pH at constant [Ni(tetren)$^{2+}$] = 1.00 x 10^{-5} M.

pH	[bipy] x 10^3 M	k^0 x 10^3 s^{-1}	pH	[bipy] x 10^3 M	k^0 x 10^3 s^{-1}
6.00	2.23	4.27 ± 0.08	5.30	0.501	5.46 ± 0.12
6.00	2.51	4.90 ± 0.14	5.30	0.612	6.27 + 0.46
6.00	2.78	5.87 ± 0.27	5.31	0.696	6.66 ± 0.12
6.02	2.98	6.60 ± 0.66	5.31	0.793	7.53 ± 0.11
6.00	3.34	7.43 ± 0.47	5.10	0.501	8.33 ± 0.36
5.70	1.11	5.77 ± 0.14	5.12	0.612	10.2 ± 0.31
5.70	1.39	6.70 ± 0.67	5.10	0.696	11.2 ± 0.44
5.70	1.53	7.02 ± 0.44	5.11	0.793	13.6*
5.70	1.67	7.40 ± 0.43	5.00	0.390	8.89 ± 0.61
5.50	0.780	5.61 ± 0.18	5.00	0.501	12.2 ± 0.60
5.50	0.947	6.61 ± 0.22	5.00	0.612	14.6 ± 0.66
5.50	1.17	7.95 ± 0.18			

Rate Constant Model

The order in bipy and hydrogen ion can be found through the following analysis. The pseudo-first-order rate constant k^0 in (8) can be written as a two term function involving both possible forms of bipy in solution, unprotonated and protonated:

$$(10)\quad k^0 = k_{\mathrm{bipy}}^{\mathrm{Ni(tetren)bipy}}[\mathrm{bipy}] + k_{\mathrm{Hbipy^+}}^{\mathrm{Ni(tetren)bipy}}[\mathrm{Hbipy^+}]$$

Taking into account the K_a expression for Hbipy$^+$, the second term is modified, and the final rearranged equation for the second-rate constant k is represented by:

$$(11)\quad k = \frac{k^0}{[bipy]} = k_{\mathrm{bipy}}^{\mathrm{Ni(tetren)bipy}} + k_{1\,\mathrm{Hbipy^+}}^{\mathrm{Ni(tetren)bipy}}[\mathrm{H^+}]$$

where the rate constant in the second term is described by:

$$(12)\quad k_{1\,\mathrm{Hbipy^+}}^{\mathrm{Ni(tetren)bipy}} = \frac{k_{\mathrm{Hbipy^+}}^{\mathrm{Ni(tetren)bipy}}}{\mathrm{K_a}}.$$

In (11) the first "k" term on the right represents the proton unassisted attack of bipy on Ni(tetren)$^{2+}$ while the second "k" corresponds to the proton assisted attack as given in (12). A plot of data provided in Table 2 according to equation (11) is shown in Figure 4, and its linearity supports assumption 2, that the order in bipy is one. For this plot, the Pearson correlation coefficient r is 0.993 over a ten-fold increase in [H$^+$], demonstrating that the order in [H$^+$] is also one. The plot is force-fitted to a y intercept of zero because the actual y intercept of -0.29 $M^{-1}s^{-1}$ obtained from linear regression is smaller than its standard error of ± 0.31.

Discussion

Based on the above results, some key insights can be made into the substitution reaction of Ni(tetren)$^{2+}$ and bipyridine. First of all, data shows that the reaction is first-order in each of the three reactants: Ni(tetren)$^{2+}$, bipy, and H$^+$, so that it is third-order overall as given in the complete rate law:

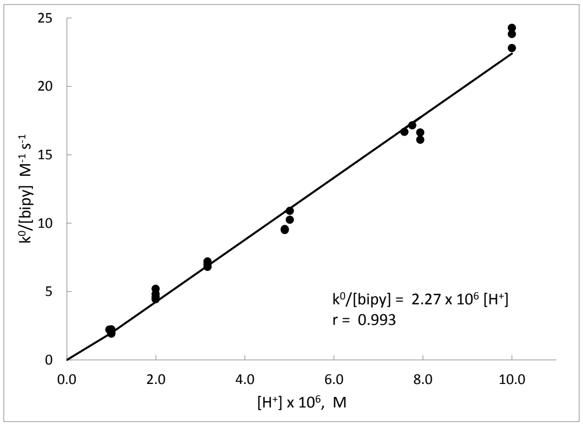

Figure 4. Plot of k^0/[bipy] vs [H$^+$] for the Ni(tetren)$^{2+}$-bipy reaction to resolve rate constants into proton assisted and unassisted terms.

$$(13)\; Rate = [Ni(tetren)^{2+}]\,[bipy]\,\{\,k_{bipy}^{Ni(tetren)(bipy)} + k_{1\,Hbipy^+}^{Ni(tetren)(bipy)}\,[H^+]\,\}$$

Secondly, the rate constant for the attack of bipy on Ni(tetren)$^{2+}$, given by the second term in curly braces, corresponding to attack on Ni(tetren)$^{2+}$ by H$^+$ is:

$$(14)\qquad k_{1\,Hbipy^+}^{Ni(tetren)bipy} = 2.27\,x\,10^6 \pm\, 5.7\,x\,10^4\, M^{-2}s^{-1}$$

where this value represents the slope of the plot in Figure 4. On the other hand, the first term in equation (13), representing the proton unassisted attack of bipy on Ni(tetren)$^{2+}$ is small and close to zero. Hence the rate law (13) reduces to:

$$(15)\quad Rate = k_{1\,\mathrm{Hbipy}^{+}}^{\mathrm{Ni(tetren)bipy}}\,[Ni(tetren)^{2+}]\,[bipy]\,[\mathrm{H}^{+}]$$

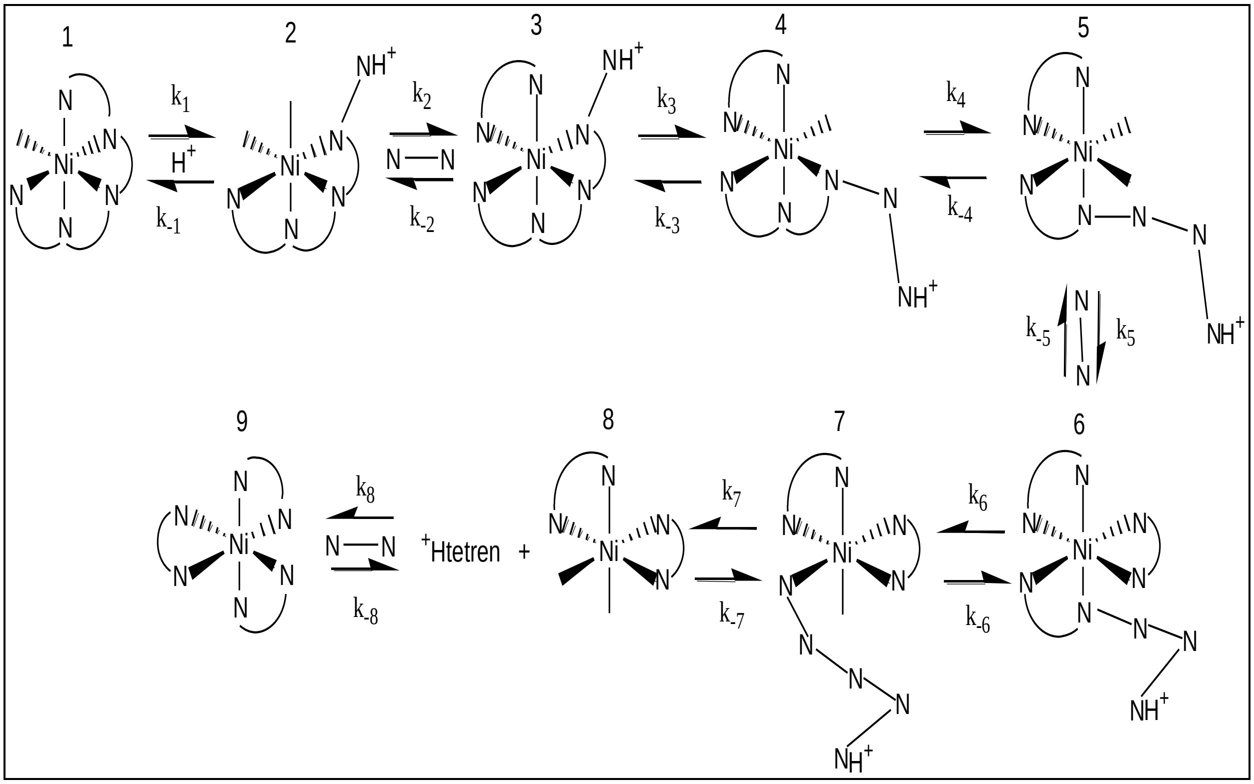

Figure 5: Proposed mechanism for the Ni(tetren)$^{2+}$-bipy ligand exchange reaction.

Thirdly, from the data gathered as well as information demonstrated through previous published research, the mechanism in Figure 5 has been proposed.

The mechanism presented in this figure is supported by the dependence of reaction rate on both [H^{+}] and [bipy] as shown in Figure 4. Additionally, this mechanism is supported by the very low substitution rate constant measured for attack of bipy directly on Ni(tetren)$^{2+}$.

An associative mechanism is ruled out because it would involve ternary complex formation, while the data obeys a non-ternary complex formation model. This conclusion is also supported by the fact that Ni(tetren)$^{2+}$ is steric hindered, and has only one open coordination site.

On the other hand, a dissociative mechanism is implausible because the first step would be slow, while the second step would be fast and independent of [bipy], and an order of zero in [bipy] would be expected.

Hence the proposed mechanism is a hybrid of associative and dissociative models in which a hydrogen ion protonates first N atom and causes it to detach from Ni(tetren)$^{2+}$, initiating a series of stepwise N dissociations, and bipy additions. This mechanism would exhibit a reaction rate dependent on both [bipy] and [H^{+}], as observed. As more nitrogen atoms detach, the rate of bipy addition would be expected to increase.

It should also be noted however, that in most nickel centered substitution reactions it is common to see formation of a ternary complex as the initial step. The results herein indicate that in more acidic solutions, where protonation of the nitrogen can occur more readily, the bipyridine can begin the substitution reaction and thus drive it to completion. From this data, it is inferred that the initial step is unlikely to be the formation of a ternary complex of the form Ni(tetren)(bipy)$^{2+}$. Although no direct experimental evidence rules out the formation of a ternary complex, the proposed model fits the kinetic data.

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