

Ligand Exchange Kinetics of 2,2'-Bipyridine with Nitrilotriacetatonickelate(II)

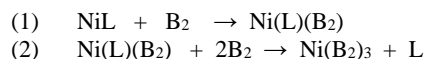
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The kinetics of the ligand exchange reaction between 2,2'-bipyridine (bipy) and NiNTA⁻ was studied over the pH range 4.7 to 7.5 at 25.0 °C and an ionic strength of 0.10 M by following the formation of Ni(bipy)₃ product at 307 nm. All reactions were run under pseudo-first order conditions with a [bipy]/[NiNTA⁻] ratio of at least 20. The reaction is first-order with respect to each of NiNTA⁻ and to bipy. The reaction is also accelerated by hydrogen ion. The rate constant for the hydrogen ion unassisted addition of bipy to NiNTA⁻ is $k_{\text{bipy}}^{\text{Ni(NTA)bipy}} = 0.671 \text{ M}^{-1} \text{ s}^{-1}$. The reaction is also first-order in hydrogen ion with a rate constant for the hydrogen ion assisted addition of bipy to NiNTA⁻ of $k_{\text{H,bipy}}^{\text{Ni(NTA)bipy}} = 9.45 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$. A dissociative type mechanism accelerated by hydrogen ion is proposed. The work has significance by showing that NiEDDA and NiNTA, both aminopolyacrylate complexes react by the same mechanism.

Keywords: Kinetics, ligand exchange, ligand substitution, 2,2'-bipyridine, NiNTA

Introduction

Ligand substitution reactions of nickel(II) complexes (NiL) ordinarily follow dissociative type mechanisms and are generally accelerated by hydrogen ion^{1,2}. When a sufficient number of coordination sites in the nickel complex reactant are initially water solvated, reactions with bidentate ligands (B₂) involve the rapid formation of a ternary complex (1) followed by a slower ligand exchange (2):



Numerous studies³⁻⁶ have examined the effects that coordinated multidentate ligands exert on the formation of ternary complexes, but fewer have described analogous effects in ligand exchange reactions. Steinhaus⁷ found that the NiEDDA-1,10-phenanthroline ligand exchange reaction followed a mechanism in which phen coordinates to a partially unwrapped NiEDDA species whereas the Ni(trien)²⁺-phen reaction⁸ showed that trien completely dissociated before phen was able to coordinate. Coordinated phen did not alter the dissociation of EDDA from Ni(EDDA)(phen) but it accelerated the dissociation of trien from Ni(trien)(phen) by a factor of 200 times that of Ni(trien)²⁺. In previously reported work on NTA, Cassatt⁹ reported that the ternary complex formation of NiNTA⁻ with phen was slightly faster than with bipy and that Hbipy⁺ reacted with NiNTA⁻ while Hphen⁺ did not. Bydlaek¹⁰ studied the metal exchange reaction between NiNTA⁻ and Cu²⁺ and found that the reaction was first-order in each reactant and in hydrogen ion. Another study¹¹ followed the reaction between Ni(trien)²⁺ and 2,2'-bipyridine, but the mechanism was not fully elucidated. Moreover, Kolopajlo et al¹² reported the reaction between Ni(tetren)²⁺ and 2,2'-bipyridine and found that it was second-order overall, and followed a linear dependence of rate constant versus hydrogen ion concentration as reported for the NiEDDA-bipy reaction; the mechanism followed a proton assisted pathway.

This report adds to the previous work done on NTA by investigating the ligand exchange reaction of NiNTA⁻ with bipy. It examines the kinetic effect of replacing an amine group in EDDA with an acetate group to give NTA whose corresponding NiNTA⁻ complex then contains three labile dentate sites compared to two in EDDA.

Aside from adding to the knowledge base of coordination chemistry kinetics, another reason for studying this reaction is that NTA is released into the environment, mainly through its many industrial and commercial uses. For example, because NTA is a better chelating agent than phosphate for both calcium and magnesium, it is used as a green water softening agent to substitute for sodium and potassium triphosphates in detergents and cleansers¹³. In another commercial use, NTA is used to extract arsenic, chromium, and copper from wood preserved with heavy metal arsenates¹⁴. On the other hand, nickel is also released to the environment from numerous anthropogenic and natural sources¹⁵, and is generally considered to exist at a concentration less than 10 µg/L in drinking water¹⁶.

Experimental

Reagents

High purity reagents (> 99%) from Aldrich Corp. were used. Nitrilotriacetic acid (Sigma grade, ≥ 99.0%), and nickel(II) hexahydrate (99.999%), were used to prepare NiNTA⁻. MES buffer (2-(N-morpholino)ethanesulfonic acid, ≥ 99.5%) was employed over the pH range 5.5 to 6.7 while HEPES buffer (4-(2-Hydroxyethyl)piperazine-1-ethanesulfonic acid, ≥ 99.5%) was used for reactions from pH 6.8 to 8.2. Water was doubly distilled and passed through a Millipore Nanopure water purification system before use. All 2,2'-bipyridine solutions were stored in the dark because they are light sensitive.

Safety

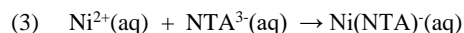
The safety precautions associated with NTA¹⁷ and nickel¹⁸ are readily found. Workers should avoid skin contact

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with 2,2'-bipyridine and NTA. Nickel nitrate is a strong oxidizer and must be stored properly. Most importantly, sodium cyanide¹⁹, used in the preparation of NiNTA described below, is lethal, and must be contained at all times in a fume hood. Because on contact with acid, it liberates hydrogen cyanide gas which is also lethal, its solutions must be maintained at pH > 10. Moreover, students should not handle or perform any procedures using NaCN.

Preparation and Standardization of NiNTA⁻

The nickel-nitrioltriacetate complex was prepared using known procedures²⁰ by adding a slight excess of Ni(NO₃)₂ to a solution of nitrilotriacetic acid with a ratio of nickel to NTA³⁻ slightly above one:



The reaction was allowed to proceed while the pH was gradually raised to about 12 using NaOH. Excess nickel was filtered off as the hydroxide using a 0.1 micron Millipore filter and the pH of the resulting complex was lowered to the range 6 to 7 for storage. The solutions were standardized by adding excess cyanide at pH 9 and measuring the concentration of Ni(CN)₄²⁻ at 267 nm.

Procedure for Kinetic Runs

All kinetic measurements were carried out at 25.0 °C, at an ionic strength (μ) of 0.10 M, and within the pH range 4.7 to 7.5 with the addition of MES or HEPES buffer, both noncomplexing reagents. The final solution pH was adjusted with sodium hydroxide or hydrochloric acid while the ionic strength of all reaction mixtures was controlled using sodium chloride. An Orion Model 290 A Plus pH meter with glass and reference electrodes was used and the pH of each reaction mixture, measured at the start and end of each reaction, held constant.

All spectral and kinetic measurements were performed in a 1 cm cell under Peltier temperature control using an Agilent Model 8453 uv/vis spectrophotometer. The increase of the product Ni(bipy)₃ absorbance was followed at 307 nm because this wavelength showed the greatest change in molar absorptivity between reactants and products. At this wavelength, the values of the molar absorptivities (M⁻¹ cm⁻¹) are listed in Table 1.

Table 1. Molar absorptivities of reacting species at 307 nm.

Compound	Molar Absorptivity, ε M ⁻¹ cm ⁻¹
Ni(bipy) ₃	3.41 x 10 ⁴
Ni(NTA)(bipy)	1.22 x 10 ⁴
Hbipy ⁺	1.01 x 10 ⁴
Bipy	4.75 x 10 ²
NiNTA ⁻	22.3

Taking into account the absorbances of all species at both time t and time infinity, the concentration of NiNTA⁻ at time t can be computed using the following equation:

$$(4) \frac{[\text{Ni}(\text{NTA})(\text{bipy})]}{b(\epsilon_{\text{Ni}(\text{bipy})_3} - 2\epsilon_{\text{bipy}} - 2[\text{H}^+] \frac{\epsilon_{\text{Hbipy}^+}}{K_a} - \epsilon_{\text{Ni}(\text{NTA})(\text{bipy})})} = \frac{A_\infty - A_t}{b(\epsilon_{\text{Ni}(\text{bipy})_3} - 2\epsilon_{\text{bipy}} - 2[\text{H}^+] \frac{\epsilon_{\text{Hbipy}^+}}{K_a} - \epsilon_{\text{Ni}(\text{NTA})(\text{bipy})})}$$

In equation (4), the two terms in the numerator represent absorbance values of Ni(bipy)₃ at time infinity and at time t whereas in the denominator, b is the pathlength, and the other terms represent the molar absorptivities of each respective species. The lower pH limit for data collection is around 4.7 because below this value, small absorbance changes were measured due to the high molar absorptivity of Hbipy⁺. In addition, the faster reactions made data collection less reproducible.

Results

The NiNTA⁻-bipy ligand exchange reaction occurs in two main steps as shown above in (1) and (2) with L = NTA and B₂ = bipy. The overall exchange reaction is given by:



in which the two coordinated water molecules occupy cis positions in NiNTA(H₂O)₂⁻. The experimental data is summarized in Table 2 where each reported rate constant along with its standard deviation represents the average of three to five runs, except for the rate constant marked with an asterisk which was obtained from duplicate runs.

Table 2. First-order rate constants for the NiNTA⁻-bipy reaction at 25.0 °C, μ = 0.10M where [NiNTA⁻] = 2.01 x 10⁻⁵ M.

pH	10 ⁴ [bipy] ₀ M	10 ⁴ k ⁰ s ⁻¹	pH	10 ⁴ [bipy] ₀ M	10 ⁴ k ⁰ s ⁻¹
7.507	4.18	2.61 ± 0.13	6.010	12.54	6.89 ± 0.18*
7.250	4.18	2.70 ± 0.070	5.757	4.18	3.24 ± 0.089
7.002	4.18	2.67 ± 0.044	5.502	4.18	3.57 ± 0.18
6.250	4.18	2.81 ± 0.007	5.250	4.18	4.20 ± 0.27
6.026	4.18	3.09 ± 0.10	5.010	4.18	4.82 ± 0.11
6.020	8.36	5.07 ± 0.13	4.767	4.18	6.31 ± 0.56
6.020	10.6	5.92 ± 0.11			

For all kinetic runs listed in Table 2, the initial bipyridine concentrations [bipy]₀ represent the total initial values while the NiNTA⁻ concentration was held constant at 2.01 x 10⁻⁵ M. Pseudo-first-order conditions were employed with at least a 20 fold excess of [bipy] over [NiNTA⁻]. All reactions were followed to at least 90% completion.

If the reaction is first-order in NiNTA⁻, then at constant pH, the following rate equation holds using the fact that [bipy]₀ >> [NiNTA⁻]:

$$(6) \text{Rate} = -\frac{d[\text{Ni}(\text{NTA})(\text{bipy})]}{dt} = \frac{d[\text{Ni}(\text{bipy})_3]}{dt} = k^0 [\text{Ni}(\text{NTA})(\text{bipy})]$$

where $k^0 = k [\text{bipy}]_0$ is the pseudo-first-order rate constant and k is the second-order rate constant. When equation (6) is integrated, a plot of $\log [\text{Ni}(\text{bipy})_3]$ versus time gave a straight-line of slope k^0 . All plots, such as the one shown in Figure 1, were linear over three half lives, establishing the reactant order in $[\text{NiNTA}^-]$ as one.

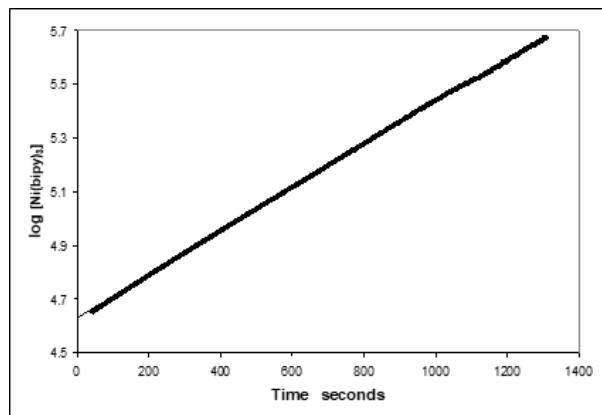


Figure 1. Plot of $\log [\text{Ni}(\text{bipy})_3]$ vs. time at pH 5.50. Bold line represents collected data points.

The absence of biphasic behavior in these first-order plots indicates the presence of NiNTA^- as the only reactant.

Having established first-order behaviour with respect to NiNTA^- , the dependence of k^0 on bipyridine concentration was studied. In solution, bipyridine can exist in unprotonated (bipy), mono-protonated (Hbipy^+) or diprotonated ($\text{H}_2\text{bipy}^{2+}$) forms. In the pH range studied, the diprotonated form is of negligible concentration. Further, because of the flexibility of bipy, the possibility exists that both the mono- and diprotonated forms may react with NiNTA^- .

To find the concentration of free bipy available to react with NiNTA^- , the total initial bipyridine concentration $[\text{bipy}]_0$, as given in Table 2, must be corrected for the amount lost in forming the ternary complex through the equation:

$$(7) [\text{bipy}]_{\text{free}} = [\text{bipy}]_0 - [\text{NiNTA}^-]_0 = [\text{Hbipy}^+] + [\text{bipy}]$$

where $[\text{bipy}]_{\text{free}}$ expresses the available bipy partitioned between the mono- and un-protonated forms. The dependence of k^0 on $[\text{bipy}]$ was studied using four runs at pH 6.0 and the corresponding data is given in Table 2. A plot of k^0 vs $[\text{bipy}]$, where bipy concentrations were calculated via a distribution diagram, is displayed in Figure 2. The plot is linear, indicating a first-order dependence on the monoprotated form of bipy.

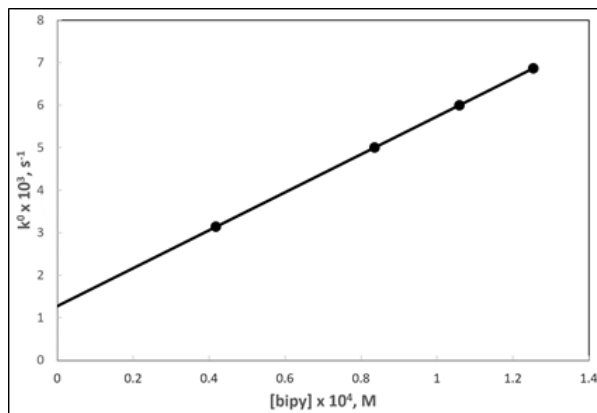


Figure 2. Plot of k^0 vs. $[\text{bipy}]$ at pH 6.0.

Experiments also demonstrated that the reaction rate decreased as the pH increased as shown by the plot of k^0 versus pH in Figure 3.

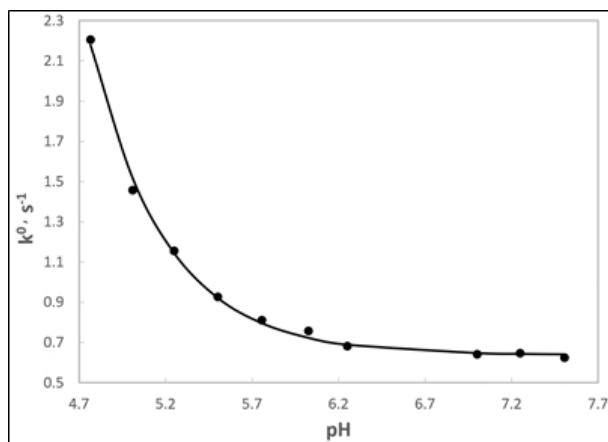


Figure 3. Dependence of rate constant k^0 on pH.

Assuming that both mono- and di-protonated bipy species are able to react with NiNTA^- , the second-order rate constant can be written as a two term function in bipy and Hbipy^+ .

$$(8) k^0 = k_{\text{bipy}}^{\text{Ni(NTA)bipy}} [\text{bipy}] + k_{\text{Hbipy}^+}^{\text{Ni(NTA)bipy}} [\text{Hbipy}^+]$$

Substituting for $[\text{Hbipy}^+]$ using its first acid dissociation constant K_a gives:

$$(9) k^0 = k_{\text{bipy}}^{\text{Ni(NTA)bipy}} [\text{bipy}] + \frac{k_{\text{Hbipy}^+}^{\text{Ni(NTA)bipy}} [\text{H}^+] [\text{bipy}]}{K_a}$$

Rearranging (8) allows the hydrogen ion dependence to be resolved:

$$(10) k = \frac{k^0}{[\text{bipy}]} = k_{\text{bipy}}^{\text{Ni(NTA)bipy}} + k_{\text{Hbipy}^+}^{\text{Ni(NTA)bipy}} [\text{H}^+]$$

where k is the second-order rate constant and

$$k_{H,bipy}^{Ni(NTA)bipy} = \frac{k_{Hbipy^+}^{Ni(NTA)bipy}}{K_a}$$

All the experimental data, including runs representing both constant pH and varying bipyridine concentrations are plotted together according to equation (9) in Figure 4. The bipyridine concentrations used in the plot were computed using the fraction of bipyridine existing in the unprotonated form using published pK_b values²¹.

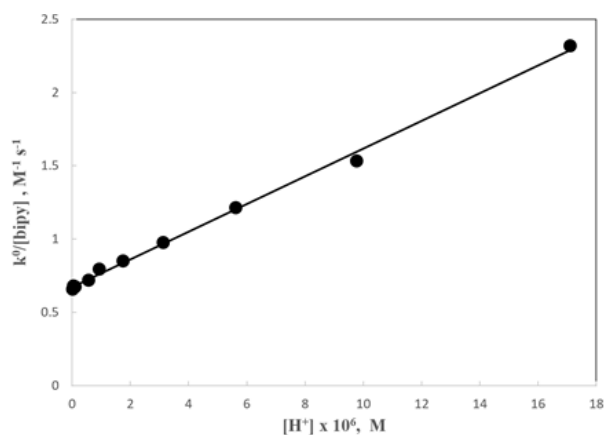


Figure 4. Resolution of proton dependent- and independent- rate constants.

The graph is linear over four orders of magnitude in hydrogen ion concentration with a correlation coefficient of 0.998. The slope obtained from the k^0 versus $[H^+]$ plot gives the proton dependent addition of bipy to NiNTA, denoted by $k_{H,bipy}^{Ni(NTA)bipy}$, while the intercept given by $k_{bipy}^{Ni(NTA)bipy}$,

Table 3. Resolved rate constants for the reactions of $X = \text{phen}$ or bipy with $NiLX$ where $L = NTA^-$, EDDA or tetren represents the hydrogen ion independent addition of bipy to NiNTA. A summary of the experimentally determined rate constants and those of similar reactions is provided in Table 3.

	$k_{H,X}^{NiLX}$ $M^{-2}s^{-1}$	k_X^{NiLX} $M^{-1}s^{-1}$
NiNTA-bipy	$(9.45 + 0.0017) \times 10^4$	$0.672 + 0.011$
NiEDDA-phen	$(5.17 \pm 0.16) \times 10^3$	$(7.84 \pm 0.18) \times 10^{-2}$
Nitetren-bipy	$2.27 \times 10^6 \pm 5.7 \times 10^4$	-0.29 ± 0.31
Rate constant ratio (NiNTA/NiEDDA)	18.3	8.6
(Nitetren/NiNTA)	25.2	Not applicable

Discussion

If in the initial nickel complex, NTA completely decoordinates before bipy attacked, then the order in bipy would be zero. However, since the reaction is first-order in bipy, the general mechanism must involve bipy attacking a partly decoordinates

NTA which is subsequently displaced. Therefore the rate determining step must occur after at least one bipy coordinates in the ternary complex and before the fast addition of the third bipy to form $Ni(bipy)_3$. The proposed mechanism, shown in Figure 5, is similar to that reported for the NiEDDA-phen reaction and the rate determining step given by $5 \rightarrow 6$, most likely involves the breakage of the nickel-glycinate bond in intermediate 5.

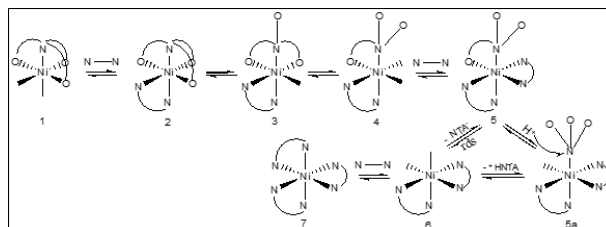


Figure 5. General mechanism for the ligand exchange reaction between bipy and NiNTA.

The increased rate at lower pH values is attributed to protonation of a partly detached NTA segment that is then unable to recoordinate to nickel. This process is shown in step $5 \rightarrow 5a$ of Figure 5. As in the NiEDDA-phen system, at lower pH values, the more basic nitrogen of the aminocarboxylate protonates first while accelerating the dissociation of the nickel complex.

The $k_{H,bipy}^{Ni(NTA)bipy}$ term is about 20 times higher than the corresponding rate constant for the NiEDDA-phen reaction. Further, the proton unassisted rate constant for the NiNTA-bipy reaction is about 8 times higher than that for the NiEDDA-phen reaction, as given in Table 3.

These differences are attributed to the more flexible attacking bipy, the more labile NiNTA, and greater steric hindrance in NiEDDA. It is possible to predict²³ the 2nd order rate constant k_{56} describing the proton unassisted addition of bipy to NiNTA by using the equation:

$$(11) \quad k_{bipy}^{Ni(NTA)bipy} = \frac{K_{Nigly^+} K_{Nibipy}}{K_{NiNTA}} K_{el} k_{Nigly}$$

The first factor in (11) takes into account the stability of intermediate 5 relative to that of the initial complex. The K_{el} term²⁴ describes the contribution of the electrostatic attraction of complexed nickel ion for glycinate, which helps stabilizes intermediate 5, while the k_{Nigly} term is the rate constant for the dissociation of glycinate from nickel. Using these values published by Martell and Smith²⁵: $K_{Nigly^+} = 1.95 \times 10^5$,

$K_{Nibipy} = 1.05 \times 10^7$, $K_{NiNTA} = 3.16 \times 10^{11}$ and this value by Hammes²⁶: $k_{Nigly} = 0.024 \text{ s}^{-1}$ along with a calculated value of $K_{el} = 3.2$ by Bydalek¹⁰, gives a predicted value of $k_{bipy}^{Ni(NTA)bipy} = 0.50 \text{ M}^{-1} \text{ s}^{-1} = k_{56}$ which compares favorably with the measured value of $0.672 \text{ M}^{-1} \text{ s}^{-1}$.

In conclusion, the kinetic behavior of the NiNTA-bipy reaction is very similar to that reported for the NiEDDA-phen reaction with proton assisted pathway dominant. Moreover, the NiNTA rate constants for proton assisted and non-assisted pathways are much higher, by a magnitude of ten. These results indicate that changing the bidentate ligand from phen to

bipy while increasing the number of labile dentate sites from two to three on going from EDDA to NTA, does not alter the mechanism which may therefore be of general utility for all aminopolycarboxylate nickel(II) complexes. However, the straight chain polyamine nickel complex of tetren is faster so that the reaction rate follows the order: NiEDDA < NiNTA < Nitetren, with the latter complex reacting about 25 times faster than NiNTA. The Nitetren reaction differs from the aminopolycarboxylate reactions in that it has only has a proton assisted pathway. Further work is underway to examine the reactions of bipy with Nitrien²⁺ and Nitren²⁺.

Acknowledgements

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