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Kinetics of the Substitution Reaction between Copper(II) and Nitrilotriacetatonickelate(II)

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The kinetics of the substitution reactions between the nitrilotriacetatonickelate(II) ion and the hydrated copper(II) and radionickel(II) ions have been studied from pH 2.6 to 4.9 with ionic strength and temperature variation. The rate of copper(II) substitution is only 12 times faster than the rate of radionickel exchange. The rate of acid dissociation is 310 times faster than the rate of copper(II) substitution. These ratios of rates are quite different from those found with the ethylenediaminetetraacetatonickelate(II) ion, 20,000 and 4.9×10^{-2}, respectively, but can be quantitatively related to these values on the basis of proposed dinuclear reaction intermediates.

Introduction

Studies of the reactions of copper(II)[1] and zinc(II)[2] with the ethylenediaminetetraacetatonickelate(II) (Ni-EDTA) ion have indicated that the reaction rates can be related to the relative stability of dinuclear EDTA reaction intermediates. Studies[3,4] involving the reactions of other similar nickel(II) complexes with copper(II) have led to the conclusion that the reaction proceeds through an intermediate having an iminodiacetate segment of the chelating agent bonded to copper(II) and a glycinate segment bonded to nickel(II). The rate step is then the breaking of the nickel–nitrogen bond. The present study investigates the effect of replacing an iminodiacetate segment of EDTA by an acetate group to give the ligand, nitrilotriacetate (NTA or L^{-3}). The copper attack, radionickel exchange, and hydrogen ion dissociation of its nickel complex (Ni-NTA or NiL^-) are studied.

The system studied is

$$NiL^- + Cu^{+2} \underset{k_{Ni}{}^{CuL}}{\overset{k_{Cu}{}^{NiL}}{\rightleftharpoons}} CuL^- + Ni^{+2} \qquad (1)$$

$$NiL^- \underset{k_{Ni}{}^{L}}{\overset{k^{NiL}}{\rightleftharpoons}} Ni^{+2} + L^{-3} \qquad (2)$$

$$NiL^- + H^+ \underset{k_{Ni}{}^{HL}}{\overset{k_H{}^{NiL}}{\rightleftharpoons}} Ni^{+2} + HL^{-2} \qquad (3)$$

$$Cu^{+2} + \begin{bmatrix} L^{-3} \\ HL^{-2} \end{bmatrix} \overset{\text{rapid}}{\rightleftharpoons} CuL^- + [H^+] \qquad (4)$$

The rate is then expressed as

$$\frac{d[CuL^-]}{dt} = k_{Cu}{}^{NiL}[Cu^{+2}][NiL^-] + k^{NiL}[NiL^-] + k_H{}^{NiL}[H^+][NiL^-] \qquad (5)$$

The rate of radionickel exchange is given by an analogous expression.

Experimental

The experimental procedures were similar to those reported previously.[1,2] Precautions were taken to avoid interferences from other complexes or from trace impurities. No buffer was used and no difficulty was encountered in maintaining constant pH during the reaction in the pH range studied. The pH of the reaction solutions was adjusted with perchloric acid. Sodium perchlorate was used to adjust the ionic strength of all solutions. Nickel and copper perchlorates were prepared from their carbonates and standardized by direct titration (using murexide indicator) against a standard EDTA solution. Reagent grade nitrilotriacetic acid, H_3NTA, was dried before use and standardized by direct titration[5] (using murexide indicator) against a primary standard copper nitrate solution. Results of these titrations agreed to within 0.3% of the theoretical value. Solutions of Ni-NTA and Cu-NTA were prepared from equimolar quantities of the metal perchlorate and NTA solutions, followed by pH adjustment to 4.5. Species such as $Cu(NTA)_2$ and $Ni(NTA)_2$ are not formed under the conditions used in the rate solutions.[6,7]

The reactions were followed spectrophotometrically at the 750 mμ absorption band of Cu-NTA. The values of $\epsilon_{Ni\text{-}NTA}$, ϵ_{Ni}, ϵ_{Cu}, and $\epsilon_{Cu\text{-}NTA}$ are 2.6, 1.9, 10.2, and 58.5, respectively, at 750 mμ. The values of $\epsilon_{Ni\text{-}NTA}$ and $\epsilon_{Cu\text{-}NTA}$ are independent of pH in the range 2.5–4.9, indicating no evidence for any acid species such as HNi-NTA.

The concentration of product at any time was calculated from the expression

$$[\text{Cu-NTA}] = \frac{A - A_i}{b(\epsilon_{Cu\text{-}NTA} + \epsilon_{Ni} - \epsilon_{Ni\text{-}NTA} - \epsilon_{Cu})} \qquad (6)$$

where A is the observed absorbance, A_i is the initial absorbance of the reactants, and the cell length, b, is 5 cm. Equation 6 assumes that there is no stable mixed complex such as $NiNTACu^+$. This assumption appears valid, since the values of the initial absorbance obtained by extrapolation to zero time agree very well with the calculated values and an isosbestic point is observed (438 mμ) when a repetitive spectral scan is made during the reaction of equimolar concentrations of reactants, thus indicating a transition from a set of reactants in rapid equilibrium to a similar set of products without any buildup of intermediates. All rate solutions contained excess nickel(II) to repress prior dissociation of the Ni-NTA. The concentration of nickel(II) in excess had no effect on the rate. The reactions were followed for at least 75% conversion to Cu-NTA and were reproducible to ±3%.

Radionickel Exchange.—Nickel nitrate solutions of known concentrations were subjected to neutron bombardment to produce Ni^{65} (half-life 2.56 hr., maximum γ-energy 1.5 Mev.). Nitrate solutions were used rather than perchlorate solutions to avoid production of radioactive Cl^{38}. The exchange reactions were initiated by the addition of a measured aliquot (containing

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[1] T. J. Bydalek and D. W. Margerum, *J. Am. Chem. Soc.*, **83**, 4326 (1961).

[2] D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **1**, 852 (1962).

[3] T. J. Bydalek and D. W. Margerum, *ibid.*, **2**, 678 (1963).

[4] D. W. Margerum and T. J. Bydalek, *ibid.*, **2**, 683 (1963).

[5] G. Numajiri, M. Kodama, and A. Shimizu, *Nippon Kagaku Zasshi*, **81**, 454 (1960); *Chem. Abstr.*, **55**, 15222*e* (1961).

[6] B. Kirson and R. Bornstein, *Bull. Soc. Chim. France*, 288 (1960).

[7] B. Kirson and R. Bornstein, *ibid.*, 1081 (1961).

TABLE I

OBSERVED FIRST-ORDER RATE CONSTANTS

25.0°, μ = 1.25, $[Cu^{+2}] = 2.32 \times 10^{-2}$ *M*

No.	pH	[Ni-NTA] $\times 10^4$, *M*	$[Ni^{+2}]$ $\times 10^4$, *M*	k_0, sec.$^{-1}$ $\times 10^4$
1	4.94	5.64	4.51	0.404
2	4.75	5.64	4.51	0.415
3	4.56	5.64	4.51	0.480
4	4.32	5.64	4.51	0.584
5	4.25	5.64	4.51	0.640
6	3.85	5.64	4.51	1.03
7	3.54	5.64	4.51	1.59
8	3.40	5.64	4.51	2.15
9	3.23	5.64	4.51	2.95
10	3.08	5.84	4.91	3.85
11	3.07	5.84	4.91	4.02
12	2.81	5.84	4.91	7.39
13	2.68	5.84	4.91	9.82
14	2.64	5.84	4.91	10.2
15	2.59	5.84	4.91	11.0
16	3.27	5.84	1.96	2.68
17	3.27	5.84	13.5	2.65
18	3.30	11.7	4.91	2.50
19	3.28	29.2	4.91	2.62
20	3.28	58.4	4.91	2.58
21	3.22	58.4	4.91	2.94

approximately 7 μcuries of Ni^{65}) of the irradiated nickel(II) solution to a solution containing Ni-NTA, excess Ni^{+2}, and Na ClO_4 in the same proportions as in the exchange rates involving copper(II). The pH was adjusted to between 5 and 5.5 to minimize the effect of the hydrogen ion dissociation path. This effect was corrected for by using the data obtained spectrophotometrically. The temperature for all experiments was 25.0°.

During the course of the reaction, 5-ml. aliquots, containing approximately 0.3 mequiv. of Ni^{+2}, were removed from the reaction solution, and the nickelous ion was separated from the complex ion by ion exchange. The aliquot was passed through a column of Dowex 50-X-8 cation resin in the Na^+ form. The nickelous ion is retained on the column and the negative Ni-NTA is rapidly eluted. The columns were 1 cm. in diameter with a 3-ml. bed volume and had a capacity of approximately 6 mequiv. The flow rate was 3 ml./min. The columns were washed free of complex with water until a final eluent volume of 13 ml. was collected in a test tube. In this volume all Ni-NTA activity could be washed from the column and the volume was large enough so that the counting geometry was constant. The separation time was negligible compared to the reaction time. Each solution was then counted in the test tube for 10 min. using a sodium iodide, thallium-activated, scintillation detector and scaling unit (Nuclear Chicago). The total counts were then corrected back to zero time using the decay constant calculated from a standard decay curve. This curve was obtained by counting an aliquot of the reaction solution without prior separation by ion exchange. Values of the decay constant agreed to within 1% of the reported value. Background corrections were also made.

The rate of exchange is given by the usual equation

$$R = \frac{-2.3ab}{a+b}\frac{\mathrm{d}}{\mathrm{d}t}\log(1-F) \qquad (7)$$

where *F* is the fractional exchange at time *t*, and *a* and *b* are the concentrations of free and complexed nickel ions. The concentration of free Ni^{+2} is the sum of the excess Ni^{+2} and the irradiated Ni^{+2} added. The rate of exchange was determined from the slope of straight line plots of log (1 − *F*) *vs.* time and was reproducible to ±5%.

Kinetics of the Forward Reaction.—In all forward rate studies the $[Cu^{+2}]$ was in large excess and constant during the rate run. The back reaction was negligible under the conditions used. The rate can be expressed as

$$-\frac{\mathrm{d[Ni\text{-}NTA]}}{\mathrm{d}t} = \frac{\mathrm{d[Cu\text{-}NTA]}}{\mathrm{d}t} = k_0\mathrm{[Ni\text{-}NTA]} \qquad (8)$$

where k_0 is the total observed first-order rate constant. Values of k_0 were obtained from typical straight line plots of log $[\mathrm{Ni\text{-}NTA}]_t$ *vs.* time. Table I shows the variation of k_0 as the pH is varied from 4.94 to 2.59 (no. 1–15) and the constancy of k_0 as the excess $[Ni^{+2}]$ (no. 16 and 17) and [Ni-NTA] (no. 18–21) are varied at a constant $[Cu^{+2}]$ of 2.32×10^{-2} *M*. Although not evident from Table I, a plot of k_0 *vs.* $[H^+]$ yields a straight line with a slope of 4.34×10^{-1} l. mole^{-1} sec.$^{-1}$ (k_H^{NiL}) and an intercept of 3.57×10^{-5} sec.$^{-1}$. The straight line dependence thus indicates a term that is first order in $[H^+]$ and the positive value of the intercept implies a second hydrogen ion independent term and/or a copper(II) dependent term.

The variation of k_0 with $[Cu^{+2}]$ is given in Table II. The values of k_0 can be corrected for their hydrogen ion contribution by subtracting out the product $k_H^{NiL}[H^+]$. These corrected values are given in the last column in Table II. A plot of these values *vs.* $[Cu^{+2}]$ yields a straight line with a slope of $1.39 \times 10^{-}$. l. mole^{-1} sec.$^{-1}$ (k_{Cu}^{NiL}) and intercept of 3.5×10^{-6} sec.$^{-1}$ (k^{NiL})[8] The straight line dependence on $[Cu^{+2}]$ indicates a term that is first order in $[Cu^{+2}]$ while the intercept indicates a term that gives the first-order dissociation of Ni-NTA independent of both $[Cu^{+2}]$ and $[H^+]$. The over-all rate can therefore be expressed as

$$\frac{\mathrm{d[Cu\text{-}NTA]}}{\mathrm{d}t} = k^{NiL}\mathrm{[Ni\text{-}NTA]} + k_H^{NiL}[H^+]\mathrm{[Ni\text{-}NTA]} + k_{Cu}^{NiL}[Cu^{+2}]\mathrm{[Ni\text{-}NTA]} \qquad (9)$$

where the values of k^{NiL}, k_H^{NiL}, and k_{Cu}^{NiL} are 3.5×10^{-6} sec.$^{-1}$, 4.34×10^{-1} l. mole^{-1} sec.$^{-1}$, and 1.39×10^{-3} l. mole^{-1} sec.$^{-1}$, respectively, at 25.0° and an ionic strength of 1.25 *M* $NaClO_4$. The error in the value of k_H^{NiL} and k_{Cu}^{NiL} is ±3%. In the case of k^{NiL}, due to its small magnitude and the fact that it is found by difference, the error is ±10%. These errors also hold for the constants measured at other ionic strengths and temperatures.

TABLE II

VARIATION OF OBSERVED RATE CONSTANT WITH $[Cu^{2+}]$

25.0°, μ = 1.25, [Ni-NTA] = 5.64×10^{-4} *M*,
$[Ni^{+2}] = 4.51 \times 10^{-4}$ *M*

No.	pH	$[Cu^{+2}]$ $\times 10^2$, *M*	k_0, sec.$^{-1}$ $\times 10^5$	$k_H^{NiL}[H^+]$, sec.$^{-1}$ $\times 10^5$	$k_0 - k_H^{NiL}[H^+]$, sec.$^{-1}$ $\times 10^5$
1	5.01	0.770	1.77	0.42	1.35
2	4.94	0.770	2.05	0.50	1.55
3	5.00	1.54	2.89	0.43	2.46
4	4.95	1.54	3.02	0.49	2.53
5[a]		2.32			3.57

[a] Value of intercept from plot of k_0 *vs.* $[H^+]$, data of Table I.

The reaction rate is only slightly affected by ionic strength in the region of high ionic strength as evidenced from rate studies performed at μ = 0.40 *M* sodium perchlorate and 25.0°. Under these conditions the values of k^{NiL}, k_H^{NiL}, and k_{Cu}^{NiL} are 5.8×10^{-6} sec.$^{-1}$, 7.69×10^{-1} l. mole^{-1} sec.$^{-1}$, and 1.84×10^{-3} l. mole^{-1} sec.$^{-1}$, respectively.

The temperature dependence of all three reaction paths was studied between 15.0 and 35.0° at an ionic strength of 1.25 by means of similar sets of kinetic measurements at these two temperatures. The results follow the Arrhenius expression and the kinetic parameters for the three constants are given in Table III.

Kinetics of the Reverse Reaction.—The kinetics of the reverse reaction were studied in the pH range 3–4 at 25° and an ionic strength of 1.25 *M* sodium perchlorate. The system is consistent in that the reverse reaction contains two terms that are first order in Ni^{+2} and Cu-NTA and inverse first order in Cu^{+2}. Likewise

TABLE III

KINETIC PARAMETERS

	E_a, kcal./mole	ΔH^*, kcal./mole at 25°	ΔS^*, e.u.
k^{NiL}	17.4	16.8	−27
$k_{\mathrm{H}}{}^{\mathrm{NiL}}$	18.3	17.7	−1
$k_{\mathrm{Cu}}{}^{\mathrm{NiL}}$	18.0	17.4	−13

one of these terms is $[H^+]$ independent while the second is $[H^+]$ dependent. The third term, corresponding to the direct interaction of Ni^{+2} and Cu-NTA, was too small to be evaluated under the conditions used. The reverse rate does not proceed to completion and this further complexity necessitated the use of a differential plot to obtain the values of the rate constants. Plots of the concentration of product, Ni-NTA, *vs.* time were made, and the rate was determined at various concentrations by taking the slope of the curve at those points. Knowing the over-all rate, the concentrations of all species, the rate of the back reaction, and the equilibrium constants for Cu-NTA and $HNTA^{-2}$, the rate constants for the reaction between Ni^{2+} and NTA^{-3} and $HNTA^{-2}$ were evaluated. These values are 4.8×10^5 and 7.5 l. mole^{-1} sec.$^{-1}$, respectively. These values are in good agreement with the values calculated on the basis of the forward rate constants and equilibrium constants for Ni-NTA and $HNTA^{-2}$. The calculated values are 6.0×10^5 and 14.7 l. mole^{-1} sec.$^{-1}$, respectively. The discrepancy between values can be attributed to the fact that the values of the stability constants used, $10^{11.26}$ and $10^{12.68}$ for Ni-NTA and Cu-NTA,[8] respectively, were for 20° and an ionic strength of 0.1 M KCl.

Radionickel Exchange.—The exchange of radioactive nickel(II) with Ni-NTA was studied at 25.0° and an ionic strength of 1.25 M sodium perchlorate. From the values of k^{NiL} and $k_{\mathrm{H}}{}^{\mathrm{NiL}}$ previously obtained, the rate of exchange due to these dissociative terms can be readily calculated. In all cases, at higher pH values, the rate of radionickel exchange is greater than this calculated rate as seen in Table IV. This portion of the rate can be explained by a term, $k_{\mathrm{Ni}}{}^{\mathrm{NiL}}[\mathrm{Ni}^{+2}][\mathrm{Ni\text{-}NTA}]$, which is analogous to the term found in the copper(II) rate. The value of $k_{\mathrm{Ni}}{}^{\mathrm{NiL}}$ is given in the last column of Table IV. As the pH is lowered, this nickel term becomes less important due to the increase in the hydrogen ion dissociative path and at pH 3.79 contributes only 5% to the reaction rate under the conditions used.

TABLE IV

RATE CONSTANTS FOR RADIONICKEL EXCHANGE

25.0°, μ = 1.25

pH	$[Ni^{+2}]$ × 10^2, M	[Ni-NTA] × 10^2, M	Obsd. rate × 10^7, M sec.$^{-1}$	Dissociative rate × 10^7, M sec.$^{-1}$	$k_{\mathrm{Ni}}{}^{\mathrm{NiL}}$ × 10^4, M^{-1} sec.$^{-1}$
5.42	3.60	2.92	2.6	1.5	1.1
5.45	3.27	2.92	2.5	1.5	1.1
5.32	2.96	2.92	2.8	1.6	1.3
5.10	3.00	4.87	5.2	3.4	1.2
3.79	3.00	0.974	7.4	7.5[a]	. . .
					Av. 1.2

[a] Total rate including the Ni^{+2} term.

Discussion

The reaction between copper(II) and Ni-NTA proceeds by reaction paths that are similar to those previously reported in the copper(II) and Ni-EDTA system. The energies of activation of the copper(II) reaction with Ni-NTA and Ni-EDTA are the same, 18.0 kcal./mole. Differences exist, however, in the order of magnitude of the various reaction paths. In the Ni-NTA system, the value of $k_{\mathrm{H}}{}^{\mathrm{NiL}}$ is 310 times larger than $k_{\mathrm{Cu}}{}^{\mathrm{NiL}}$, whereas in the Ni-EDTA system, the value of $k_{\mathrm{H}}{}^{\mathrm{NiY}}$ is one-twentieth as large as $k_{\mathrm{Cu}}{}^{\mathrm{NiY}}$. Likewise the difference between $k_{\mathrm{H}}{}^{\mathrm{NiL}}$ and $k_{\mathrm{H}}{}^{\mathrm{NiY}}$ and between $k_{\mathrm{Cu}}{}^{\mathrm{NiL}}$ and $k_{\mathrm{Cu}}{}^{\mathrm{NiY}}$ can be examined.

These comparisons of rate constants can be made in terms of calculated intermediate stability constant ratios for the various Ni-NTA and Ni-EDTA reaction intermediates as previously described.[3] A comparison of this type is possible only if it is assumed that the rate step in each reaction intermediate is identical. Under these conditions, the experimental rate constant (*e.g.*, $k_{\mathrm{Cu}}{}^{\mathrm{NiL}}$) can be written as a product of the stability constant of the reaction intermediate (K_{NiLCu}) and the rate constant for breaking the nickel ion away from this intermediate (k^{NiLCu}).

$$k_{\mathrm{Cu}}{}^{\mathrm{NiL}} = K_{\mathrm{NiLCu}} k^{\mathrm{NiLCu}} \qquad (10)$$

The value of the intermediate stability constant (K_{NiLCu}) is calculated from the relative stability constant (K_{R}) corrected for statistical and electrostatic effects. The relative stability constant of each intermediate is calculated from the equilibrium stability constants of the incoming ion and the nickel ion segments and compared to the equilibrium stability of the initial nickel complex.

$$K_{\mathrm{R}} = \frac{K_{\text{incoming ion segment}} K_{\text{Ni segment}}}{K_{\text{Ni complex}}} \qquad (11)$$

In some cases, an electrostatic attraction of an unbound acetate group tends to stabilize one structure relative to another. Correction is made for this effect using eq. 12.

$$\Delta F_{\text{electrostatic}} = \frac{Z_A Z_B e^2}{D r_{AB}} = 2.3RT \log K_{\mathrm{el}} \qquad (12)$$

A value of $\log K_{\mathrm{el}} = 0.5$ is obtained for this stabilization using r_{AB} as 6 Å. from models and the dielectric constant for water. Statistical corrections are made by considering the number of different ways each intermediate can form. Since ratios of intermediate stability constants are used throughout, no attempt has been made to present absolute values for these constants.

Table V gives the preferred structures and the calculated intermediate stability constant ratios for the various Ni-NTA reaction intermediates. The structures are chosen on the basis that: (1) five-membered rings are most stable and (2) the rate step in each species is identical. The good agreement between predicted and observed rate constant ratios indicates that the rates can be predicted on the basis of dinuclear reaction intermediates having one acetate group bonded to the incoming ion. The bonding to nickel is shown as the glycinate on the basis of a following comparison to the Ni-EDTA system. The fact that both Cu^{+2} and Ni^{+2} direct reactions proceed through identical reaction intermediates indicates that the rate of water loss from the incoming nickel ion is not kinetically important as opposed to its possible importance in the radionickel exchange with Ni-EDTA. This is as expected, since

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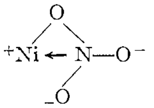
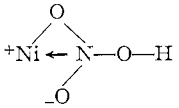
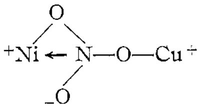
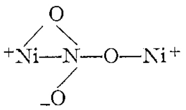
[8] J. Bjerrum, S. Schwarzenbach, and L. G. Sillén, "Stability Constants, Part I. Organic Ligands," The Chemical Society, London, 1957.

Table V

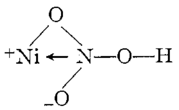
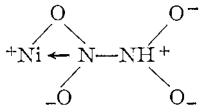
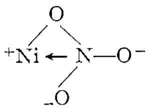
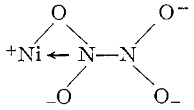
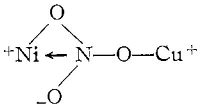
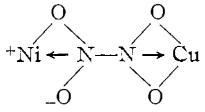
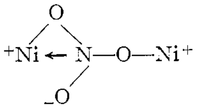
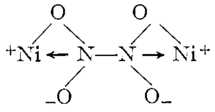
Preferred Structures and Relative Stabilities of Ni-NTA Reaction Intermediates

	Structure	Predicted ratio of rate constants	Observed ratio
(1)	 log K_R = −5.97[a] log K_{el} = 0.5[b]	$\frac{K_{NiL^-}}{K_{NiLH}} = \frac{k^{NiL}}{k_H{}^{NiL}} = 3.6 \times 10^{-5}$	8.0×10^{-6}
(2)	 log K_R = −1.33[a]	$\frac{K_{NiLH}}{K_{NiLCu}} = \frac{k_H{}^{NiL}}{k_{Cu}{}^{NiL}} = 9.8 \times 10^2$	3.1×10^2
(3)	 log K_R = −4.32[a]	$\frac{K_{NiLCu}}{K_{NiLNi}} = \frac{k_{Cu}{}^{NiL}}{k_{Ni}{}^{NiL}} = 10$	12
(4)	 log K_R = −5.30[a]		

[a] Values of log K_R are based on the following stability constants taken from ref. 8 to match temperature and ionic strengths as nearly as possible: NiL, 11.26; Ni acetate, 0.67; Cu acetate, 1.65; acetic acid, 4.64; Ni glycinate, 5.29 (the latter value is based on hydroxyethylethylaminoacetate as a model). [b] Statistical factor of $^1/_2$ when compared to structure 2.

Table VI

Comparison of Ni-NTA and Ni-EDTA Reaction Intermediates

	Ni-NTA	Ni-EDTA	Predicted ratio NTA:EDTA	Observed ratio
(1)	 log K_R = −1.33[a] statistical factor of $^3/_2$	 log K_R = −3.62[a]	2.9×10^2	5.4×10^2
(2)	 log K_R = −5.97[a] statistical factor of $^3/_4$	 log K_R = −13.27[a]	2.0×10^7 Predicted $k^{NiY} = 2.9 \times 10^{-13}$ sec.$^{-1}$ [c] $= 1.8 \times 10^{-13}$ sec.$^{-1}$ [d]	Not obsd.
(3)	 log K_R = −4.32[a] statistical factor of $^3/_2$	 log K_R = −2.18[a]	1.1×10^{-2}	8.5×10^{-2}
(4)	 log K_R = −5.30[a] statistical factor of $^6/_8$	 log K_R = −7.98[a] log K_{el} = −0.5	1.1×10^2	1.5×10^2

[a] Values of log K_R are based on the following stability constants and those listed in Table V. All are taken from ref. 8 to match temperature and ionic strengths as closely as possible: Ni-EDTA, 18.56; Cu-iminodiacetate, 11.09[b]; H-iminodiacetate, 9.65.[b] [b] Values based on methyliminodiacetate complexes. Values of $k_H{}^{NiY}$, $k_{Ni}{}^{NiY}$, and $k_{Cu}{}^{NiY}$ used are 8×10^{-4}, 8×10^{-7}, and 1.63×10^{-2} M^{-1} sec.$^{-1}$, respectively, from C. M. Cook, Jr., and F. A. Long, *J. Am. Chem. Soc.*, **80**, 33 (1958), and ref. 1. [c] Value calculated from the predicted ratio, 2.0×10^7, and the value of k^{NiL}. [d] Value calculated from the predicted ratio, 2.2×10^{-10}, between EDTA structures 1 and 2 and the value of $k_H{}^{NiY}$.

only one bond is formed to the incoming nickel ion in the Ni-NTA intermediate.

The increase in the value of $k_H{}^{NiL}$ over k^{NiL} is also explained on the basis of the proposed reaction intermediates. Furthermore, the observed ratio is essentially identical with the ratio of rate constants observed in the Cd-NTA dissociation.[9] The ratio $k_H{}^{CdL}/k^{CdL}$ is 7.4

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(9) N. Tanaka, K. Ebata, T. Takahari, and T. Kumagai, *Bull. Chem. Soc. Japan*, **35**, 1836 (1962).

$\times 10^4$ as compared to 7.5×10^4 for the Ni-NTA system. The values of k_H^{CdL} and k^{CdL} are 2.5×10^5 M^{-1} sec.$^{-1}$ and 3.4 sec.$^{-1}$, respectively. No direct comparison can be made between these values and the corresponding Ni-NTA values because of differences in the rate step. The identical ratio, however, shows that the Cd-NTA dissociation follows a similar path to that found in the Ni-NTA dissociation. In the Cd-NTA system a second-order hydrogen ion dependence was also observed at high acidities. Failure to observe this term in the Ni-NTA system might be due to the fact that a high enough acidity was not reached.

Besides comparing the various Ni-NTA intermediates, direct comparison can also be made between the Ni-NTA and the Ni-EDTA systems on the basis that the rate step is identical in the two systems. Table VI makes this comparison and shows the good agreement obtained. The replacement of an iminodiacetate group by an acetate group does not alter the rate step but does affect the magnitude of the rate constant since the stability of the reaction intermediate is altered. This change in rate constant is quantitatively explained on the basis of the proposed dinuclear reaction intermediates.

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Coordination Compounds of Nickel(II) Salts with Substituted Pyridines. Square-Planar, Tetrahedral, and Octahedral Compounds of 3,4- and 3,5-Dimethylpyridine

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The preparation of a series of new coordination compounds of nickel(II), containing 3,4- and 3,5-lutidine (dimethylpyridines) and various anions (Cl^-, Br^-, I^-, NCS^-, NO_3^-, ClO_4^-, BF_4^-) is reported. Compounds with square-planar, tetrahedral, and octahedral stereochemistry were obtained. Their configurations were deduced from their magnetic and spectral properties. Unusual complexes containing coordinated ClO_4^- and BF_4^- are reported.

Introduction

This work is a continuation of previously reported studies on the coordination compounds of nickel(II) with substituted pyridines.[1,2] For general information concerning the dimethylpyridines (lutidines) as ligands in metal complexes and in particular the aims of this research, we refer to our paper on the nickel(II) complexes of the α-substituted lutidines.[2]

Experimental

Starting Materials.—The 3,4- and 3,5-lutidine (3,4-L and 3,5-L or simply L) and the anhydrous nickel(II) halides and thiocyanate were purified as described in the previous paper.[2] The infrared spectra of the purified lutidines agreed with those reported in the literature.[3] The acetonitrile complexes of nickel(II) perchlorate and tetrafluoroborate were obtained from their respective hydrated nickel(II) salts by repeated crystallization from acetonitrile–ethyl ether.

Preparation of the Complexes.—The compounds prepared, together with their colors, melting or decomposition temperatures, and magnetic moments, are listed in Table I.

TABLE I
FORMULAS AND SOME PHYSICAL PROPERTIES OF SOLID NICKEL(II)–β-LUTIDINE COMPLEXES

Compound	Color	μ_{eff}, B.M.[a]
$[Ni(3,4\text{-}L)_4Cl_2]$	Green	3.13
$[Ni(3,5\text{-}L)_4Cl_2]$	Bluish green	3.19
$[Ni(3,4\text{-}L)_4Br_2]$	Green	3.32
$[Ni(3,4\text{-}L)_2Br_2]$	Blue-violet	3.60
$[Ni(3,5\text{-}L)_4Br_2]$	Bluish green	3.23
$[Ni(3,4\text{-}L)_4]I_2$	Yellow-brown	Diamag.
$[Ni(3,5\text{-}L)_4I_2]$	Yellow	3.29
$[Ni(3,4\text{-}L)_4(NCS)_2]$	Light blue	3.18
$[Ni(3,5\text{-}L)_4(NCS)_2]$	Light blue	3.12
$[Ni(3,4\text{-}L)_4(NO_3)_2]$	Blue	3.25
$[Ni(3,5\text{-}L)_4(NO_3)_2]$	Blue	3.20
$[Ni(3,4\text{-}L)_4](ClO_4)_2$	Yellow	Diamag.
$[Ni(3,5\text{-}L)_4(ClO_4)_2]$	Light blue	3.27
$[Ni(3,4\text{-}L)_4](BF_4)_2$	Yellow	Diamag.
$[Ni(3,5\text{-}L)_4(BF_4)_2]$	Light blue	3.26

[a] At 20°. Diamagnetic corrections were made.

The complexes of the general formula NiL_4X_2 (X = Cl, Br, I, NCS, NO_3) were prepared as previously described for the halide, thiocyanate, and nitrate complexes of the other lutidines.[2] The complexes of 3,4-L are readily soluble in, and were recrystallized from, dichloromethane; those of 3,5-L are only sparingly soluble and were not recrystallized. Most of the complexes decompose on heating, often without melting, in the range 100–200°. In some cases, a change of color is observed well below the decomposition

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[1] M. D. Glonek, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **84**, 2014 (1962).

[2] S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 480 (1964).

[3] E. A. Coulson, J. D. Cox, E. F. G. Herington, and J. F. Martin, *J. Chem. Soc.*, 1934 (1959).