

ridine ring occurs. Unlike the back donation of electrons in pyridine oxide which occurs through the ring π system, the back donation of electrons in this chelate appears to be distributed in the pyridine ring by the σ bonds. Another possible exception to the structure A_1 is bis(thiopicolinamidato)nickel(II), in which the low

steric requirements of the hydrogens could allow the formation of structure A_2 . Although the solution ultraviolet spectrum of this compound supports structure A_2 , the magnetic data and solubility indicate that this material is polymeric in the solid phase, presumably due to interchelate coordination.

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

BY T. J. BYDALEK AND A. HETZEL CONSTANT

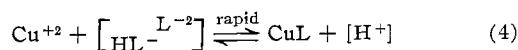
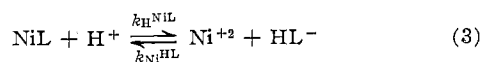
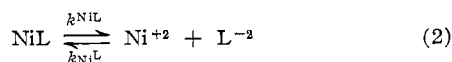
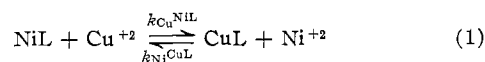
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The kinetics of the substitution reaction between the monoiminodiacetatonickelate(II) ion and the hydrated copper(II) ion have been studied from pH 4.9 to 3.4 with ionic strength and temperature variation. The over-all rate of reaction is given by the expression $R = k_{Cu}^{NiL} [Cu^{+2}] [NiL] + k^{NiL} [NiL] + k_H^{NiL} [H^+] [NiL]$ where $[NiL]$ refers to the concentration of the monoiminodiacetatonickelate(II) ion. The rate expression is similar to that for copper exchange with the nitrilotriacetatonickelate(II) ion¹ and is quantitatively related to this rate on the basis of proposed reaction intermediates assuming an identical rate step in each system, *i.e.*, the breaking of the nickel-nitrogen bond.

Introduction

The reaction of copper(II) with the nitrilotriacetatonickelate(II) ion¹ has been measured and postulated to proceed through an intermediate possessing an acetate group bonded to copper(II) and a glycinate segment bonded to nickel(II). The rate-determining step involves the breaking of the nickel-nitrogen bond. The third acetate group of the ligand was assumed to be nonbonded but contributed to the stability of the intermediate by electrostatic attraction. The present study investigates the effect of replacing this acetate group by a proton, giving the ligand, iminodiacetate (ImDA or L^{-2}). The copper attack and hydrogen ion dissociation of its nickel complex (Ni-ImDA or NiL) are studied.

The system is



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. Nickel and copper perchlorates were prepared from their carbonates and standardized by direct titration (using murexide indicator) against a standard EDTA solution. Iminodiacetic acid was precipitated by the addition of hydrochloric acid to a solution of the disodium salt (Eastman). The acid was further recrystallized three times from water and standardized as a monoprotic acid³ by pH titration with standard sodium hydroxide solution. Results of these titrations agreed to within 0.5% of the theoretical value. In the rate studies, solutions of ImDA were prepared just prior to use to avoid possible bacterial decay. Nickel perchlorate was then added in excess to assure the formation of the mono complex⁴ and the pH adjusted to 5. The reaction was begun by the addition of an acidic copper perchlorate solution.

The reaction was followed spectrophotometrically at the 725 $m\mu$ absorption band of Cu-ImDA. The values of ϵ_{NiL} , ϵ_{Ni} , ϵ_{Cu} , and ϵ_{CuL} are 1.8, 2.1, 8.4, and 70.2 $M^{-1} \text{ cm}^{-1}$, respectively, at 725 $m\mu$. The values of ϵ_{NiL} and ϵ_{CuL} are independent of pH in the range 5.0 to 3.4, indicating no evidence for any acid species such as HNi -ImDA.

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

$$[Cu\text{-ImDA}] = \frac{A - A_i}{b(\epsilon_{CuL} + \epsilon_{Ni} - \epsilon_{NiL} - \epsilon_{Cu})} \quad (5)$$

where A is the observed absorbance, A_i is the initial absorbance of the reactants, and the cell length, b , is 5 cm. The absorbance measurements were made against a blank solution containing an equivalent copper concentration as the rate solution. Equation 5 assumes that there is no stable mixed complex such as $NiImDACu^{+2}$. This assumption appears valid since the values of the initial absorbance obtained by extrapolation to zero time agree very well with the theoretical values. All rate solutions

(1) T. J. Bydalek and M. L. Blomster, *Inorg. Chem.*, **3**, 667 (1964).

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

(3) S. Chaberek, Jr., and A. E. Martell, *ibid.*, **74**, 5052 (1952).

(4) J. Bjerrum, S. Schwarzenbach, and L. G. Sillén, "Stability Constants, Part I. Organic Ligands," The Chemical Society, London, 1957.

contained excess nickel(II) to repress prior dissociation of the Ni-ImDA. This excess concentration has no effect on the rate. The reactions were followed for at least 50% conversion to Cu-ImDA and rate constants were reproducible to $\pm 3\%$.

Results

Kinetics of the Forward Reaction.—In all forward rate studies the $[\text{Cu}^{+2}]$ was in excess and constant to within 10% during the rate run. This maximum variation at the lowest copper(II) concentrations does not cause a large variation in rate constant since only a fraction of the rate proceeds through a $[\text{Cu}^{+2}]$ dependent path. The back reaction was negligible under the conditions used. The rate can then be expressed

$$\frac{-d[\text{NiL}]}{dt} = \frac{d[\text{CuL}]}{dt} = k_0[\text{NiL}] \quad (6)$$

where k_0 is the total observed first-order rate constant. Values of k_0 were obtained from typical straight line plots of $\log [\text{NiL}]$ vs. time. Table I shows the variation of k_0 as the pH is varied from 4.90 to 3.47 (no. 1-7) and the constancy of k_0 as the excess $[\text{Ni}^{+2}]$ (no. 8-10) and $[\text{NiL}]$ (no. 11-13) are varied at a constant $[\text{Cu}^{+2}]$ of $4.13 \times 10^{-3} M$. A plot of k_0 vs. $[\text{H}^+]$ yields a straight line with a slope of $1.20 M^{-1} \text{sec}^{-1}$ and an intercept of $2.60 \times 10^{-4} \text{sec}^{-1}$. The straight line dependence indicates a term that is first order in $[\text{H}^+]$,

TABLE I
OBSERVED FIRST-ORDER RATE CONSTANTS
 $\mu = 1.25, [\text{Cu}^{+2}] = 4.13 \times 10^{-3} M$

No.	pH	$[\text{NiL}]$ $\times 10^4$, M	$[\text{Ni}^{+2}]$ $\times 10^3$, M	k_0 $\times 10^4$, sec^{-1}
25°				
1	4.90	8.98	3.39	2.75
2	4.15	8.98	3.39	3.38
3	4.05	8.98	3.39	3.66
4	3.90	8.98	3.39	4.16
5	3.67	8.98	3.39	5.18
6	3.57	8.98	3.39	5.88
7	3.47	8.98	3.39	6.63
8	3.90	8.98	2.53	4.13
9	3.90	8.98	5.54	4.03
10	3.90	8.98	8.68	4.07
11	4.00	1.80	4.11	3.84
12	4.00	2.69	4.02	3.80
13	4.01	4.49	3.84	3.75
15°				
1	4.63	8.98	3.39	0.95
2	4.10	8.98	3.39	1.06
3	3.94	8.98	3.39	1.40
4	3.61	8.98	3.39	1.87
5	3.53	8.98	3.39	2.12
6	3.43	8.98	3.39	2.50
35°				
1	4.69	8.98	3.39	7.82
2	3.89	8.98	3.39	10.7
3	3.68	8.98	3.39	12.5
4	3.49	8.98	3.39	15.4

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 $[\text{Cu}^{+2}]$ is given in Table II. The values of k_0 can be corrected for their hydrogen ion contribution by subtracting out the product $k_{\text{H}^{\text{NiL}}}[\text{H}^+]$. These corrected values are given in the last column of Table II. A plot of these values vs. $[\text{Cu}^{+2}]$ yields a straight line with a slope of $2.0 \times 10^{-2} M^{-1} \text{sec}^{-1}$ ($k_{\text{Cu}^{\text{NiL}}}$) and an intercept of $1.7 \times 10^{-4} \text{sec}^{-1}$ (k^{NiL}). The straight line dependence on $[\text{Cu}^{+2}]$ indicates a term that is first order in $[\text{Cu}^{+2}]$ while the intercept indicates a term that gives the first-order dissociation of Ni-ImDA independent of both $[\text{Cu}^{+2}]$ and $[\text{H}^+]$. The over-all rate can then be expressed as

$$\frac{d[\text{CuL}]}{dt} = (k_{\text{Cu}^{\text{NiL}}}[\text{Cu}^{+2}] + k^{\text{NiL}} + k_{\text{H}^{\text{NiL}}}[\text{H}^+])[\text{NiL}] \quad (7)$$

The values of $k_{\text{Cu}^{\text{NiL}}}$, k^{NiL} , and $k_{\text{H}^{\text{NiL}}}$ are $2.0 \times 10^{-2} M^{-1} \text{sec}^{-1}$, $1.7 \times 10^{-4} \text{sec}^{-1}$, and $1.20 M^{-1} \text{sec}^{-1}$, respectively, at 25.0° and an ionic strength of 1.25 M maintained with NaClO_4 . The error in the values of $k_{\text{H}^{\text{NiL}}}$ and $k_{\text{Cu}^{\text{NiL}}}$ is $\pm 3\%$. Due to the small magnitude of k^{NiL} and the fact that it is found by difference, the error is $\pm 10\%$. These errors also hold for the constants evaluated at other ionic strengths and temperatures.

TABLE II
VARIATION OF OBSERVED RATE CONSTANT WITH Cu^{+2}
 $\mu = 1.25, \text{NiL} = 8.98 \times 10^{-4} M, \text{Ni}^{+2} = 3.39 \times 10^{-3} M$

No.	pH	$[\text{Cu}^{+2}]$ $\times 10^3$, M	k_0 $\times 10^4$, sec^{-1}	$k_0 - k_{\text{H}^{\text{NiL}}}$ $[\text{H}^+]$ $\times 10^4$, sec^{-1}
25°				
1 ^a		4.13		2.60
2	4.07	4.72	3.68	2.66
3	4.02	5.90	3.91	2.77
4	4.04	14.8	5.87	4.78
5	4.13	23.6	7.27	6.38
6	4.49	29.5	8.16	7.77
15°				
1 ^a		4.13		0.81
2	4.00	5.90	1.34	0.88
3	4.07	14.7	1.80	1.41
4	4.00	29.5	2.69	2.23
35°				
1	4.20	2.95	8.2	6.7
2 ^a		4.13		7.4
3	4.00	5.90	10.8	8.4
4	4.00	8.85	11.7	9.3
5	4.08	14.7	14.7	12.7

^a Value of intercept from plot of k_0 vs. $[\text{H}^+]$, data of Table I.

The data given for 15 and 35° in Tables I and II can be treated in an analogous manner to those at 25°. The values of $k_{\text{Cu}^{\text{NiL}}}$, k^{NiL} , and $k_{\text{H}^{\text{NiL}}}$ are $5.4 \times 10^{-3} M^{-1} \text{sec}^{-1}$, $5.7 \times 10^{-5} \text{sec}^{-1}$, and $4.6 \times 10^{-1} M^{-1} \text{sec}^{-1}$, respectively, at 15°, and $5.1 \times 10^{-2} M^{-1} \text{sec}^{-1}$, $5.2 \times 10^{-4} \text{sec}^{-1}$, and $2.45 M^{-1} \text{sec}^{-1}$, respectively, at 35°. These constants hold at an ionic strength of 1.25 M maintained with NaClO_4 . The results follow the Arrhenius expression and the kinetic parameters for

the three rate constants are given in Table III. The error in the values of E_a is 1 kcal./mole.

TABLE III
KINETIC PARAMETERS

	E_a , kcal./mole	A $\times 10^{-11}$
k_{NiL}^{NiL}	20	0.76 sec. ⁻¹
k_H^{NiL}	15	6.0 M^{-1} sec. ⁻¹
k_{Cu}^{NiL}	20	90. M^{-1} sec. ⁻¹

Similar sets of experiments were performed at 25.0° and an ionic strength of 0.1 M maintained with $NaClO_4$. The reaction is only slightly affected by this large change in ionic strength. The values of k_{Cu}^{NiL} , k_{NiL}^{NiL} , and k_H^{NiL} are $2.4 \times 10^{-2} M^{-1} \text{sec.}^{-1}$, $2.8 \times 10^{-4} \text{sec.}^{-1}$, and $2.8 M^{-1} \text{sec.}^{-1}$, respectively.

Kinetics of the Reverse Reaction.—The kinetics of the reverse reaction were followed in the pH range 3.5 to 4.5 at 25° and an ionic strength of 1.25 M maintained with sodium perchlorate. From a knowledge of the forward rate, the reverse rate can readily be expressed as

$$R = \frac{d[NiL]}{dt} = k_{Ni}^{CuL}[Ni^{+2}][CuL] + k_{Ni}^L[Ni^{+2}][L^{-2}] + k_{Ni}^{HL}[Ni^{+2}][HL^{-}] \quad (8)$$

Since the concentrations of L^{-2} and HL^{-} are governed by the Cu-ImDA equilibrium the rate can also be written as

$$R = k_{Ni}^{CuL}[Ni^{+2}][CuL] + k_{Ni}^L K_{CuL}[Ni^{+2}][CuL]/[Cu^{+2}] + k_{Ni}^{HL} K_{CuL} K_{HL}[H^+][Ni^{+2}][CuL]/[Cu^{+2}] \quad (9)$$

Under the conditions used, the first term, corresponding to the direct interaction of Ni^{+2} and CuL , was too small to be evaluated. Table IV gives the values of the rate as determined from the slope of plots of product, NiL , vs. time and the calculated concentrations of all species at the same time.

TABLE IV

RATE OF REVERSE REACTION AT 25°, $\mu = 1.25^a$

No.	R	$R[Cu^{+2}]/$	pH	$[Cu^{+2}]$	$[CuL]$	$[NiL]$	$[Ni^{+2}]$
	$\times 10^7$ $M^{-1} \text{sec.}^{-1}$	$\times 10^7$ $M^{-1} \text{sec.}^{-1}$		$\times 10^4$ M	$\times 10^4$ M	$\times 10^4$ M	$\times 10^2$ M
1	4.66	1.30	4.07	2.13	7.61	1.37	8.58
2	4.72	1.36	3.96	2.18	7.56	1.42	8.58
3 ^b	3.70	1.57	3.71	3.42	8.08	0.90	8.58
4	3.12	0.68	3.95	1.73	8.01	0.97	4.29

^a Initial concentrations: $[CuL] = 8.98 \times 10^{-4} M$; excess $[Cu^{+2}] = 7.6 \times 10^{-5} M$. ^b Excess $[Cu^{+2}] = 2.52 \times 10^{-4} M$.

Slopes were evaluated from the initial portions of the rate to avoid complications from the reverse rate. From eq. 9, the value of $R[Cu^{+2}]/[CuL]$ should be a linear function of $[H^+]$ at constant $[Ni^{+2}]$. From such a plot the slope, $2.4 \times 10^{-4} \text{sec.}^{-1}$, is equal to $k_{Ni}^{HL} K_{CuL} K_{HL}[Ni^{+2}]$. From the values⁴ of K_{CuL} and K_{HL} , $10^{10.55}$ and $10^{-9.12}$, respectively, and $[Ni^{+2}]$, the value of k_{Ni}^{HL} is readily evaluated to be $7.7 \times 10^{-2} M^{-1} \text{sec.}^{-1}$. From the intercept, $1.09 \times 10^{-7} \text{sec.}^{-1}$, the

value of k_{Ni}^L is readily calculated to be $4.5 \times 10^4 M^{-1} \text{sec.}^{-1}$. The first-order $[Ni^{+2}]$ dependence is readily seen by a comparison of no. 2 and 4 in Table IV. The values obtained for k_{Ni}^L and k_{Ni}^{HL} are in excellent agreement with the values calculated from the forward rate constants and the values of the equilibrium constants⁴ for Ni-ImDA ($10^{8.26}$) and HImDA, evaluated at an ionic strength of 0.1 M KCl and 30°. The calculated values are $3.1 \times 10^4 \text{sec.}^{-1}$ and $1.6 \times 10^{-1} M^{-1} \text{sec.}^{-1}$. From the equilibrium position of the reverse reactions, an equilibrium constant of 1.9×10^2 was calculated for the reaction of Ni-ImDA with Cu^{+2} . This compares with the value of 1.95×10^2 calculated from the ratio of equilibrium constants of Cu-ImDA to Ni-ImDA.

Discussion

Both the monoiminodiacetonickelate(II) and nitrilotriacetatonickelate(II)¹ reactions with copper(II) proceed through three reaction paths, one a simple first-order dissociation, the second a $[H^+]$ dependent dissociation, and the third a direct copper(II) attack on the nickel chelate. The magnitude of these paths can be compared on the basis of proposed reaction intermediates formed prior to the transition state assuming an identical rate-determining step in both systems. A comparison of the copper reactions with nitrilotriacetatonickelate(II) and with ethylenediaminetetraacetatonickelate(II) indicates that the nitrilotriacetatonickelate(II) reaction proceeds through a reaction intermediate possessing an acetate segment bonded to copper and a glycinate segment bonded to nickel. The most reasonable interpretation of the data for the ethylenediaminetetraacetatonickelate(II) system⁵ indicates that the breaking of the nickel-nitrogen bond is the rate-determining step. Similar intermediates were postulated for the other paths. A similar comparison between the monoiminodiacetonickelate(II), nitrilotriacetatonickelate(II), and ethylenediaminetetraacetatonickelate(II) can be made if an identical rate-determining step is assumed for all systems.

In all pathways the intermediate formed prior to the transition state has a glycinate segment of the chelating agent bonded to nickel. Analogous to the ethylenediaminetetraacetatonickelate(II) system⁵ it is assumed that the breaking of the nickel-nitrogen bond is the rate-determining step. The remainder of the chelating agent is either nonbonded or bonded to either H^+ or the incoming metal ion depending on the pathway being considered. The bonding to the incoming metal ion is considered to be the maximum possible as long as five-membered rings are formed and steric hindrance⁶ is not a factor.

Comparisons based on calculations similar to those previously reported^{1,5} have been made and they predict reasonably well the relative importance of the various pathways. For the iminodiacetate and nitrilotriacetate systems, the following ratios of ImDA:NTA rate constants are predicted: dissociation path, 70;

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

hydrogen ion dissociation path, 35; and copper attack, 35. The observed ratios are 48, 2.8, and 14, respectively. Similarly, from calculations, the hydrogen ion dependent rate constant should be 1.4×10^3 times larger than the simple first-order dissociation. The observed value is 7.1×10^2 times larger. Comparison^{1,5} can also be made between the iminodiacetate and the ethylenediaminetetraacetate systems. For the copper paths, a value of 1.2 is predicted for the ratio of ImDA:EDTA rate constants, and this value is observed. Agreement for the hydrogen ion dissociation path is not as good. A value of 1×10^4 is predicted for the ratio of ImDA:EDTA rate constants and 1.5×10^3 is observed.

The rate constants for the nickel iminodiacetate,

nitritotriacetate, and ethylenediaminetetraacetate systems can therefore be related on the basis of postulated intermediates formed prior to the transition state, and reasonable agreement is obtained between predicted and observed values. Moreover, it is reasonable that the above method of calculation can be applied to other nickel chelate systems capable of similar intermediate formation.

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Transition Metal Ion Complexes of Trimethylamine N-Oxide

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The ligand trimethylamine N-oxide has been utilized in the synthesis of a series of complexes of transition metal perchlorates. X-Ray powder pattern, conductance, magnetic, solid and solution infrared, and electronic spectral data have been utilized to determine the stereochemistries of the complexes. The spectrochemical parameters Dq and β have been calculated for the chromium(III) and cobalt(II) complexes and the Dq values compared with those previously reported.

Introduction

In recent years there have been a number of reports of transition metal complexes containing oxygen-coordinated ligands. These ligands have been utilized to form complexes of various stereochemistries, with tetrahedral, octahedral, square-planar, and intermediate cases having been reported. Ligands such as substituted and unsubstituted pyridine N-oxides,³⁻⁵ dimethyl sulfoxide,^{5b,6} amides,⁷⁻⁹ phosphine oxides,^{10,11} alcohols,¹² and hexamethylphosphoramide¹³ are among the many which have been found to participate in the formation of stable transition metal ion complexes.

It was of interest to us to prepare some complexes of the ligand trimethylamine N-oxide, so that the structures and spectrochemical parameters of such complexes could be compared with those above. In this connection it should be noted that in all complexes except those of the alcohols there is a possibility for a π -bonding interaction involving the oxygen lone-pair electrons and the ligand atom adjacent to oxygen. This interaction can then remove electron density from the oxygen, thus decreasing its donor strength. Since this possibility is not present in trimethylamine N-oxide, a comparison of the coordination chemistry of this ligand with the aforementioned oxygen donors is therefore of interest.

A few complexes of trimethylamine N-oxide have been reported. Issleib and Kreibich¹⁴ have reported complexes of trimethylamine N-oxide with cobalt halides and nitrates and manganese bromide. Cobalt chloride, bromide, or nitrate is reported to form complexes of the type CoL_2X_2 (where L is the ligand $(\text{CH}_3)_3\text{NO}$). Cobalt iodide forms the complex $[\text{L}_3\text{CoI}]\text{I}$, and the perchlorate forms $[\text{CoL}_4](\text{ClO}_4)_2$.

Kida¹⁵ has reported the synthesis of complexes of cobalt, zinc, and cadmium nitrates—and also cobalt and zinc perchlorates—with trimethylamine N-oxide.

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(2) N.S.F. Coop Fellow, 1964-1965.

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