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The Metal-Exchange Reaction between Bis(iminodiacetato-*N*,*O*,*O′*)nickelate(II) and Copper(II)

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The reaction between copper(II) and bis(iminodiacetato)nickelate(II) was studied between pH 3.7 and 4.5 over a 200-fold variation in copper concentration at an ionic strength of 1.25 and a temperature of 25 °C. The reaction consisted of two steps, the first of which involves the exchange of IDA between $Ni(IDA)_2^{2-}$ and copper, the latter step being the exchange of the remaining IDA between NiIDA and copper. The first step shows an order shift in copper from first to zero and back to first and goes through two dinuclear intermediates as the copper concentration is varied. The second step shows only first-order behavior in copper and has one dinuclear intermediate. For both steps, evidence is given for a stepwise unwrapping mechanism followed by copper attack to give a dinuclear intermediate. The presence of coordinated IDA is shown to slow down all rate constants for the first step by a factor of about 30 relative to their predicted values. A general mechanism is presented which is consistent with all the kinetic data. Comparisons to other nickel–ligand exchange reactions with copper are made and are used to show how the structure of the dinuclear intermediate determines whether order shift in attacking metal occurs or not.

Introduction

The study of metal-exchange reactions continues to be of interest.[1] Although the exchange of multidentate ligands from one metal to another has been thoroughly studied, the effect that an already coordinated ligand has upon the exchange reaction has not been investigated. The effect of a coordinated ligand upon formation rates has received considerable attention[2] and suggests valuable information can be gained by studying coordinated ligand effects upon exchange reactions.

The reaction chosen for investigation is the exchange of iminodiacetate (IDA) between nickel(II) and copper(II). The bis form of the nickel complex allows study of the effect that a coordinated IDA has upon the exchange of another IDA. The reaction between NiIDA and copper has been studied[3] and provides necessary data for the elucidation of the rate constants of the reaction between $Ni(IDA)_2^{2-}$ and copper.

The reaction proceeds in two steps, shown in eq 1 and 2.

$$Ni(IDA)_2^{2-} + Cu^{2+} \rightleftarrows NiIDA + CuIDA \tag{1}$$

$$NiIDA + Cu^{2+} \rightleftarrows Ni^{2+} + CuIDA \tag{2}$$

Reaction 1, eq 1, involves shifts in the rate-determining step which are dependent upon the copper concentration, similar to other metal-exchange systems.[1d,4] Reaction 2, eq 2, however, does not show this behavior. Rate constants for the first step are shown to be affected by the coordinated IDA. Comparison between the present system and other aminocarboxylate exchange studies shows the structure of the dinuclear intermediate dictates whether shifts in the rate-determining step occur or not.

Experimental Section

Reagents. IDA was purified by two recrystallizations from a hot basic aqueous solution with the addition of enough hydrochloric acid to effect precipitation. It was standardized by potentiometric titration against a carbonate-free sodium hydroxide solution. Solutions of $Ni(ClO_4)_2$ and $Cu(ClO_4)_2$ were prepared from G. F. Smith metal salt hexahydrates and standardized by titration against a standard solution of EDTA. A solution of $Ni(IDA)_2^{2-}$ was prepared by adding a 5% molar excess of standard $Ni(ClO_4)_2$ to a standard solution of IDA containing a 2:1 molar ratio of IDA to nickel followed by the addition of NaOH to pH 11. The excess nickel hydroxide was filtered, and the pH of the solution was adjusted to 8.

The $Ni(IDA)_2^{2-}$ solution was standardized spectrophotometrically at pH 9 by measurement of the absorbance of the complex at 578 nm. The molar absorptivity was obtained from standard nickel perchlorate and an amount of standard IDA in a 5% excess of twice as many moles of nickel. Solutions of $Cu(IDA)_2^{2-}$, CuIDA and NiIDA were prepared and standardized in a corresponding manner.

All other chemicals were reagent grade and were used without further purification. All solutions were prepared with deionized distilled water.

Equilibrium and Kinetic Measurements. All pH measurements were made on a Beckman Model 110 research pH meter with a NaCl reference electrode. All spectrophotometric measurements were made on a Cary Model 14 spectrophotometer.

A spectral study of all products and reactants showed the greatest change in molar absorptivity between reactants and products to be at 685 nm. All kinetic measurements were made at this wavelength. The molar absorptivities measured at 685 nm, $\mu = 1.25$ M, and 25 °C are as follows: $Ni(ClO_4)_2$, 1.85; $Cu(ClO_4)_2$, 5.19; $Ni(IDA)_2^{2-}$, 1.84; $Cu(IDA)_2^{2-}$, 40.1; CuIDA, 73.1.

The rate of reactions 1 and 2 was studied by following the increase in absorbance due to the formation of CuIDA. No buffer was used since there was no net change in the number of protons involved in the reaction. This was demonstrated by mixing reactants and monitoring pH as the reaction proceeded. The copper concentration was varied from 4.9×10^{-4} to 1.0×10^{-1} M while the $Ni(IDA)_2^{2-}$ concentration varied from 2.5×10^{-5} to 4.2×10^{-4} M. The reaction was studied over the pH range of 3.69–4.51. All data were obtained at 25.0 ± 0.1 °C and $\mu = 1.25$ M with 10-cm cells. A 0–0.1 absorbance slide-wire was used when small changes in absorbance were encountered.

Results

The change in absorbance of the reaction can be shown to be proportional to the change in the $Ni(IDA)_2^{2-}$ concentration. Plots of $-\ln (A_\infty - A_t)$ vs. time showed an initial curve followed by a linear portion, suggesting a consecutive step type of mechanism, shown in eq 3. Assuming this to be the case, we

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{3}$$

can derive[5] eq 4 where a_1 and a_2 are comprised of rate con-

$$A_\infty - A_t = a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) \tag{4}$$

stants and molar absorptivities. The smaller rate constant can be obtained from the linear portion of the plot. A plot of ln

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[1] (a) E. Mentasti and E. Pelizzetti, *Inorg. Chem.*, **17**, 3133 (1978); (b) D. W. Margerum, G. C. Cayley, D. C. Weatherburn, and G. K. Pagenkopf, *ACS Monogr.*, **No. 174**, 163 (1978); (c) R. K. Steinhaus and C. L. Barsuhn, *Inorg. Chem.*, **13**, 2922 (1974); (d) R. K. Steinhaus and R. L. Swann, *ibid.*, **12**, 1855 (1973).

[2] D. W. Margerum, G. C. Cayley, D. C. Weatherburn, and G. K. Pagenkopf, *ACS Monogr.*, **No. 174**, 106 (1978).

[3] T. J. Bydalek and H. Constant, *Inorg. Chem.*, **4**, 833 (1965).

[4] D. W. Margerum, D. L. Janes, and H. M. Rosen, *J. Am. Chem. Soc.*, **87**, 4464 (1965).

[5] R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition-Metal Complexes", Allyn and Bacon, Boston, Mass., 1974, pp 20–23.

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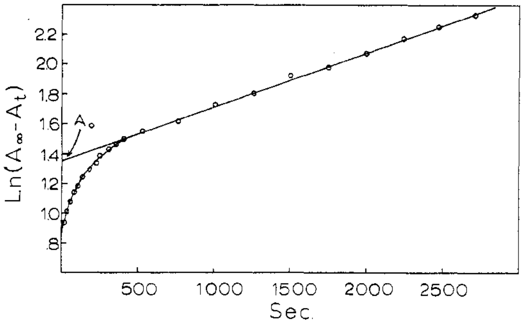

Figure 1. Typical first-order kinetic plot for $Ni(IDA)_2$–Cu reaction.

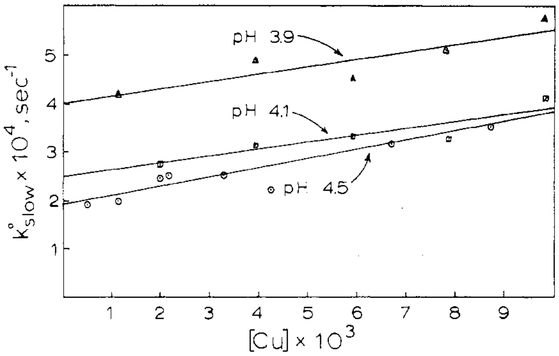

Figure 2. Effect of varying pH and copper concentration upon k_{slow} (μ = 1.25 M, 25 °C). For the sake of clarity, only selected pH values are plotted.

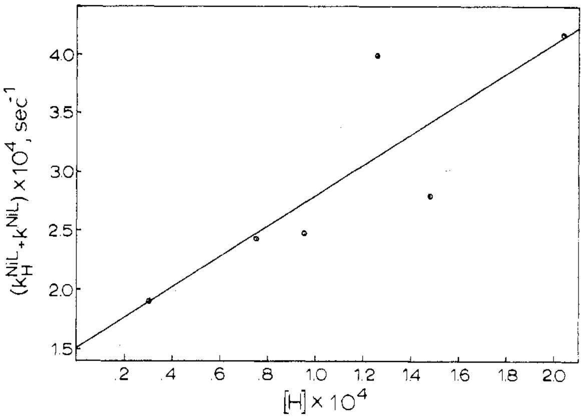

Figure 3. Resolution of $k_{diss}{}^{NiIDA}$ into proton-dependent and proton-independent terms.

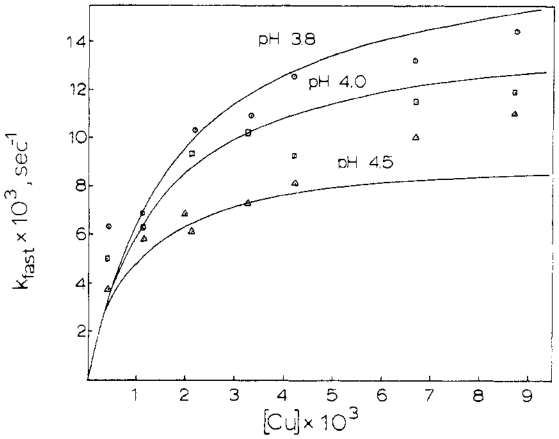

Figure 4. Effect of varying pH and copper concentration at low copper concentrations upon k_{fast} (μ = 1.25 M, 25 °C). For the sake of clarity, only selected pH values are plotted.

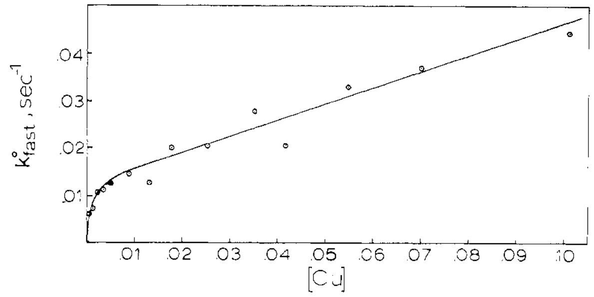

Figure 5. Effect of copper concentration upon k_{fast} at pH 3.8 (μ = 1.25 M, 25 °C).

$(A_\infty - A_t - A_0)$ vs. time for those points on the curved portion of the original plot will be linear if the mechanism is consistent with consecutive first-order reactions. A_0 is the extrapolated intercept of the original plot. The faster rate constant can be obtained from the slope of the second plot.

Figure 1 is a plot of the results of a typical run treated as described above. The plots thus demonstrated first-order dependence in $Ni(IDA)_2{}^{2-}$ for both the slow and fast steps. At least three runs at each set of concentrations and pH were made, and average values of k_{slow} and k_{fast} were calculated from these data.

The rate constants k_{fast} and k_{slow} can be assigned to the following steps:

$$Ni(IDA)_2{}^{2-} + Cu^{2+} \xrightarrow{k_{fast}} NiIDA + CuIDA \quad (5)$$

$$NiIDA + Cu^{2+} \xrightarrow{k_{slow}} Ni^{2+} + CuIDA \quad (6)$$

Extrapolation of the initial curved portion of plots like those shown in Figure 1 to the point where the line becomes parallel to the time axis, corresponding to what would be an A_∞ for that reaction, agrees well with that predicted by assuming NiIDA and CuIDA as products. Further, the observed A_∞, seen at the end of the reaction, agrees well with that predicted by assuming Ni^{2+} and CuIDA as products. Finally, the values of k_{slow} obtained in the present study agree well with values obtained by Bydalek and Constant, who studied only the reaction shown in eq 2.

Resolution of the Rate Data. The effect that a change in copper concentration has upon k_{slow} is shown in Figure 2 at several pH values. Table I lists the data. Although not shown in Figure 2, the copper concentration was increased up to 0.1 M at pH 3.8 which is three times higher than that used by Bydalek and Constant. A linear dependence was found throughout the entire copper concentration range which is in marked contrast with the NiEDDA–Cu[1d] and NiEDTA–Cu[4] systems. Values of $k^{NiIDA}{}_{Cu}$ were calculated from the slopes of the plots like those in Figure 2. The intercept of these plots is a copper-independent term for the dissociation of NiIDA. These intercepts are plotted vs. hydrogen ion concentration as shown in Figure 3, which allows resolution of $k^{NiIDA}{}_H$ and k^{NiIDA}. The overall rate for the slow step may therefore be expressed as

$$-d[NiIDA]/dt = (k^{NiIDA}{}_{Cu}[Cu^{2+}] + k^{NiIDA}{}_H[H^+] + k^{NiIDA})[NiIDA] \quad (7)$$

Comparisons of the values found in this study with those obtained by Bydalek and Constant are given in Table II.

The effect of copper concentration upon k_{fast} is shown in Figure 4 at several pH values. Figure 5 shows the copper concentration extended up to 0.1 M. The copper dependence for the fast reaction is similar to that found in the NiEDDA–Cu[1d] and NiEDTA–Cu[4] systems and in marked contrast to that found in the NiBPEDA–Cu,[1c] Ni(trien)–Cu,[6] and NiI-

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(6) P. J. Menardi, Doctoral Dissertation, Purdue University, 1966.

Table I. Variation of the Observed First-Order Rate Constants for Reactions 1 and 2 with Respect to pH and Excess Copper Ion Concentration (μ = 1.25 M, 25 °C)

pH	$10^4[Ni(IDA)_2^{2-}]$, M	$10^3[Cu^{2+}]$, M	$10^2 k_{fast}$, s^{-1}	$10^4 k_{slow}$, s^{-1}
3.70	1.90	1.96	1.23	4.25
3.67	1.90	3.92	1.39	4.77
3.70	1.90	5.88	1.67	4.53
3.68	1.90	7.84	1.98	4.93
3.83	0.245	0.491	0.631	2.44
3.82	0.494	1.09	0.686	2.60
3.80	0.816	2.17	1.03	3.34
3.84	1.66	3.30	1.09	3.27
3.79	1.98	4.21	1.25	3.79
3.84	3.26	6.67	1.32	3.44
3.84	4.12	8.74	1.44	4.85
3.80	4.12	13.4	1.27	5.44
3.85	4.12	17.5	1.98	6.05
3.82	4.12	34.9	2.73	7.34
3.83	4.12	41.5	2.02	7.94
3.85	4.12	54.7	3.27	11.5
3.82	4.12	70.0	3.71	14.5
3.83	4.12	101.0	4.45	18.3
3.87	0.494	1.09	0.573	4.18
3.90	1.90	3.92	1.68	4.87
3.91	1.90	5.88	1.43	4.52
3.90	1.90	7.84	1.73	4.97
3.90	1.90	9.80	1.81	5.77
3.87	4.12	13.4	1.37	5.92
3.87	4.12	17.5	1.88	6.75
4.03	0.250	0.496	4.86	2.19
4.04	0.494	1.13	6.17	2.21
4.02	1.00	2.11	9.34	3.11
4.02	1.75	3.25	10.20	3.54
4.01	2.00	4.21	9.25	3.02
4.01	3.24	6.66	11.5	3.53
4.03	4.21	8.72	11.9	3.80
4.03	4.21	13.3	13.9	4.18
4.08	0.250	0.496	4.08	2.20
4.11	1.90	1.96	7.55	2.72
4.20	1.90	3.92	9.56	3.13
4.11	1.90	5.88	9.35	3.33
4.15	1.90	7.84	11.8	3.27
4.10	1.90	9.80	11.7	4.10
4.50	0.250	0.496	3.73	1.92
4.49	0.494	1.13	5.88	1.98
4.51	1.90	1.96	6.85	2.45
4.50	1.00	2.11	6.09	2.53
4.45	1.75	3.25	7.32	2.53
4.50	2.00	4.21	8.16	2.21
4.52	3.24	6.66	10.1	3.17
4.52	4.21	8.72	11.0	3.53
4.54	4.21	13.3	13.6	4.20

Table II. Resolved Rate Constants for Slow and Fast Reactions (μ = 1.25 M, T = 25 °C)

Slow Reaction

constant	*a*	*b*
$k^{NiIDA}{}_{Cu}$, M^{-1} s^{-1}	$(1.48 \pm 0.33) \times 10^{-2}$	2.00×10^{-2}
$k^{NiIDA}{}_{H}$, M^{-1} s^{-1}	1.20 ± 0.15	1.20
k^{NiIDA}, s^{-1}	$(1.51 \pm 0.15) \times 10^{-4}$	1.7×10^{-4}

Fast Reaction

constant	*a*
$k^{Ni(IDA)_2}{}_{Cu}$, M^{-1} s^{-1}	10.1 ± 1.3
$k'^{Ni(IDA)_2}{}_{Cu}$, M^{-1} s^{-1}	$(3.30 \pm 0.57) \times 10^{-1}$
$k^{Ni(IDA)_2}{}_{H}$, M^{-1} s^{-1}	$(8.46 \pm 1.2) \times 10^{1}$
$k^{Ni(IDA)_2}$, s^{-1}	$(6.85 \pm 0.90) \times 10^{-3}$

[a] This study. [b] Reference 3.

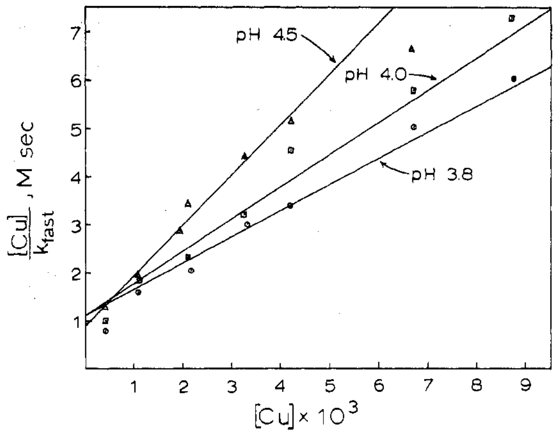


Figure 6. Resolution of k_{fast} into terms $k^{Ni(IDA)_2}{}_{Cu}$ and $k_{diss}{}^{Ni(IDA)_2}$ at varying pH values. For the sake of clarity, only selected pH values are plotted.

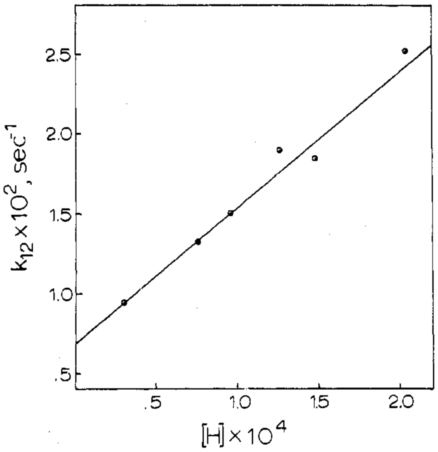


Figure 7. Resolution of $k_{diss}{}^{Ni(IDA)_2}$ into proton-dependent and proton-independent terms.

DA–Cu systems. Following systems showing similar copper dependency,[1d,4] we can use eq 8 to resolve the data at low

$$k_{fast} = \frac{k^{Ni(IDA)_2}{}_{Cu} k_{diss}{}^{Ni(IDA)_2}[Cu^{2+}]}{k_{diss}{}^{Ni(IDA)_2} + k^{Ni(IDA)_2}{}_{Cu}[Cu^{2+}]} \qquad (8)$$

copper concentration, up to 0.02 M. Adherence of the data to a rearranged form of eq 8, shown in eq 9, demonstrates that

$$\frac{[Cu^{2+}]}{k_{fast}} = \frac{1}{k^{Ni(IDA)_2}{}_{Cu}} + \frac{[Cu^{2+}]}{k_{diss}{}^{Ni(IDA)_2}} \qquad (9)$$

the curvature is the result of a shift from first- to zero-order dependence in copper. Figure 6 shows plots of eq 9 at several pH values. An average value of $k^{Ni(IDA)_2}{}_{Cu}$ can be calculated from the intercepts of Figure 6 which are essentially constant and, thus, pH independent. The slopes of the lines of Figure 6, which are pH dependent, allow calculation of $k_{diss}{}^{Ni(IDA)_2}$. A plot of $k_{diss}{}^{Ni(IDA)_2}$ vs. pH is shown in Figure 7 and reveals a proton-independent and a proton-dependent term. Equation 10 describes the plot. Analogous to the NiEDDA–Cu[1d] and

$$k_{diss}{}^{Ni(IDA)_2} = k^{Ni(IDA)_2} + k^{Ni(IDA)_2}{}_{H}[H^+] \qquad (10)$$

NiEDTA–Cu[4] systems, the two terms on the right-hand side of eq 10 represent a partial unwrapping of the ligand prior to attack by copper but not a complete dissociation of the ligand from the complex. The experimental values for the resolution of k_{fast} are shown in Table II.

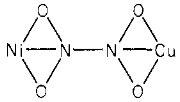
At higher copper concentration, Figure 5 shows the appearance of a second first-order term in copper. The slope of the linear portion of the plot allows calculation of this rate constant, $k'^{Ni(IDA)_2}{}_{Cu}$. The value is shown in Table II.

Discussion

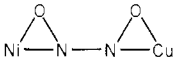
Structure of Dinuclear Intermediates. Previous studies of metal-exchange reactions have shown that these reactions involve a copper-dependent pathway which proceeds through

Table III. Comparison of NiIDA–Cu and NiL–Cu Reaction Intermediates[a]

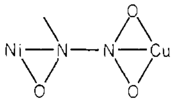
Part I



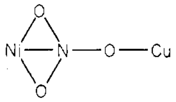
Ni(EDTA)Cu
$K_r = 1.50$



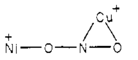
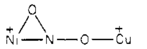
Ni(EDDA)Cu
$K_r = 1.91$



Ni(HEEDTA)Cu
$K_r = 0.179$



Ni(NTA)Cu
$K_r = 0.0222$

structures to be tested	K_r	$K_r^{\mathrm{Ni(IDA)Cu}}/K_r^{\mathrm{Ni(EDTA)Cu}}$	$K_r^{\mathrm{Ni(IDA)Cu}}/K_r^{\mathrm{Ni(EDDA)Cu}}$	$K_r^{\mathrm{Ni(IDA)Cu}}/K_r^{\mathrm{Ni(HEEDTA)Cu}}$	$K_r^{\mathrm{Ni(IDA)Cu}}/K_r^{\mathrm{Ni(NTA)Cu}}$
1 	5.78	$638^{b,c,e}$	$1000^{d,e}$	$1.07 \times 10^{4\ d,e}$	$5.76 \times 10^{4\ c-e}$
2 	0.236	$3.1 \times 10^{-2\ b,e}$	$4.9 \times 10^{-2\ e}$	0.526^{e}	$2.82^{c,e}$
$k^{\mathrm{NiIDA}}{}_{\mathrm{Cu}}/k^{\mathrm{NiL}}{}_{\mathrm{Cu}}$		0.197	0.211	0.987	10.6

Part II

complex	K_{stab}	M	$K^{\mathrm{NiL}}{}_{\mathrm{Cu}}$, $M^{-1}\ s^{-1}$
$\mathrm{NiEDTA^{2-}}$	3.31×10^{18}	Cu	1.6×10^{-2} [f]
$\mathrm{NiHEEDTA^{-}}$	1.25×10^{17}	Cu	1.5×10^{-2} [g]
NiEDDA	4.46×10^{13}	Cu	7.5×10^{-2} [h]
$\mathrm{NiNTA^{-}}$	3.16×10^{11}	Cu	1.39×10^{-3} [i]
$\mathrm{Ni(IDA)_2{}^{2-}}$	1.25×10^{14}	Cu	10.1,[j] 0.368[j]
NiIDA	1.34×10^{8}	Cu	1.48×10^{-2} [j]
$\mathrm{Ni(glycine)^{+}}$	6.03×10^{5}		
$\mathrm{NiNH_3{}^{2+}}$	5.01×10^{2}		
$\mathrm{Ni(acetate)^{+}}$	5.5		
CuIDA	3.71×10^{10}		
$\mathrm{Cu(glycine)^{+}}$	1.41×10^{8}		
$\mathrm{CuNH_3{}^{2+}}$	1.99×10^{4}		
$\mathrm{Cu(acetate)^{+}}$	5.25×10^{1}		

[a] K_r values are based on the stability constants given in part II of the table and chosen to be as internally consistent as possible with respect to temperature and ionic strength. The experimental ratios of rate constants are based upon the rate constants given in part II and at 25 °C and $\mu = 1.25$ M. All values taken from ref 11 except as noted. Statistical and electrostatic factors follow those of ref 10. [b] Statistical factor of 1/2. [c] Statistical factor of 2/3. [d] $k^{\mathrm{NiOAc}}/k^{\mathrm{NiNH_3}} = 830$. [e] $K_{\mathrm{el}} = 2.51$. [f] Reference 4. [g] Reference 10. [h] Reference 1d. [i] Reference 19. [j] This work. Value of 0.368 is $k'^{\mathrm{Ni(IDA)_2}}{}_{\mathrm{Cu}}$.

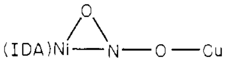
a dinuclear intermediate unless sterically hindered.[1,7-9] Further, some systems showed a shift in the order dependence upon copper from first to zero and back to first,[1d,4] while others did not.[1c,3,6] These systems have been characterized as proceeding through a weakly bonded Ni–L–Cu intermediate at high copper concentration which then rearranges to form the dinuclear intermediate found at low copper concentration. The present system involves the two reactions shown in eq 1 and 2. Reaction 1 shows the complex order dependence in copper whereas reaction 2 does not. In both reactions, copper must be involved either during or before the rate-determining step. Due to the extreme lability of copper formation reactions, compared to dissociation rates of nickel complexes, pure bond formation to copper cannot be rate limiting. Previous metal-exchange studies have shown that the structure of the dinuclear intermediate immediately prior to the rate-determining step may be characterized by a comparison of rate constant ratios involving similar systems to relative stability constant ratios for the same systems[10] as shown in eq 11, assuming the same rate-determining step to hold for both systems

$$k^{\mathrm{NiIDA}}{}_{\mathrm{Cu}}/k^{\mathrm{NiL}}{}_{\mathrm{Cu}} = K_r^{\mathrm{Ni(IDA)Cu}}/K_r^{\mathrm{Ni(L)Cu}} \tag{11}$$

where $K_r = K_{\text{Ni-segment}}K_{\text{Cu-segment}}/K_{\text{Ni-complex}}$.

The reaction shown in eq 2 has previously been analyzed in this fashion.[3] Since then, several more Ni–L–Cu systems have been characterized by following eq 11, and more accurate values for stability constants have been calculated as a result of computer-calculated data. Table III lists the comparisons between the known structures and two dinuclear intermediate structures for reaction 2, the slow reaction. Electrostatic and statistical factors are included where appropriate. Structure II involves cleavage of a nickel–acetate bond as the rate-determining step whereas all the structures to which it is being compared have nickel–nitrogen bond breakage as rate determining. A factor of 830 is used to compensate for this difference and is obtained from the ratio of nickel–acetate dissociation, $5 \times 10^3\ \mathrm{s^{-1}}$,[13] and nickel–ammonia dissociation, 6 $\mathrm{s^{-1}}$. Structure II gives the closest agreement between experimental and predicted ratios and is the same as that proposed in the earlier study.[3] Other structures were tested and caused severe disagreement between the predicted and experimental values of eq 11.

Reaction 1 involves two intermediates, one at low copper concentration and one at high copper concentration. A consideration of the unwrapping of IDA from a metal shows that only two reasonable possibilities exist for these intermediates.



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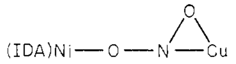

II

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(7) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **2**, 683 (1963).
(8) D. W. Margerum, P. J. Menardi, and D. L. Janes, *Inorg. Chem.*, **6**, 283 (1967).
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(12) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17** (1964); **No. 25** (1971).
(13) H. Hoffman, *Ber. Bunsenges. Phys. Chem.*, **73**, 432 (1969).
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A structure involving both acetate arms bonded to copper with the nitrogen remaining bonded to nickel would involve a highly unstable eight-member ring. No evidence for the presence of such a structure exists in other systems. The only other possible structures would involve an acetate remaining bonded to nickel and an acetate bonded to copper with a free nitrogen dentate site, or an acetate remaining bonded to nickel and a nitrogen bonded to copper with a free acetate dentate site. It is unreasonable to suggest the existence of free dentate sites as they have not been found to exist in other similar aminopolycarboxylate systems like the present one.

The coordinated IDA not undergoing an exchange may also be partially dissociated in the intermediate. Structures I and II can be written with the second IDA completely coordinated or partially uncoordinated.

Structure I would be the first intermediate to form because it involves the least amount of unwrapping. This intermediate is analogous to those found in the NiEDDA–Cu and NiEDTA–Cu systems at high copper concentration involving a weakly bonded Cu–acetate segment of the unwrapping ligand. The rate constant found at high copper concentration in this study, $k^{\mathrm{Ni(IDA)_2}}{}_{\mathrm{Cu}}$, is assigned to the formation of structure I. Rate constant $k^{\mathrm{Ni(IDA)_2}}{}_{\mathrm{Cu}}$ is thus assigned to the formation of structure II at low copper concentration.

Table IV shows a comparison of dinuclear intermediate relative stability constant ratios and rate constant ratios for structure I and various other known systems. The coordinated IDA not undergoing an exchange may also be partially dissociated in the intermediates. As shown in Table IV, structure I is tested for both a fully coordinated and partially coordinated IDA. The rate-determining step is a nickel–nitrogen bond cleavage in both forms of structure I and in all known systems. Neither of the two forms of structure I gives good agreement with rate constant ratios. However, the effect that the coordinated IDA has upon nickel–ligand bond dissociation is unknown and thus cannot be included in the relative stability constant ratios. Table V shows the same type of comparisons for two forms of structure II, the intermediate formed at low copper concentration. Structure II involves cleavage of a nickel–acetate bond as the rate-determining step and, as was done for structure I of the slow reaction, a factor of 830 is used to compensate for this difference. Again, as in Table IV, neither form of structure II gives good agreement with the rate constant ratios.

Comparison of the differences between the predicted relative stability constant ratios and the experimental rate constant ratios in both Tables IV and V shows that for structure Ib of Table IV and for structure IIa of Table V, the rate constant ratios are low by about a factor of 30 in all cases. Structure Ia of Table IV and structure IIb of Table V yield rate constant ratios that are either too high by a factor of 25 or too low by a factor of 10^4. The similarity of the factor of 30 difference found between the value of the relative stability constant ratio and the rate constant ratio for structures Ib of Table IV and IIa of Table V suggests that these two structures are the actual dinuclear intermediates through which reaction 1 proceeds. The presence of the coordinated IDA somehow slows down the exchange rate by a factor of about 30. The other possibilities mentioned above as dinuclear intermediate structures and disregarded for various reasons were also tested but not included in the tables. Agreement between their relative stability constant ratios and the rate constant ratios were very widespread.

General Mechanism. Knowledge of the structures of the dinuclear intermediates allows a mechanism to be postulated for the metal exchange of Ni(IDA)$_2$ and copper. This is shown in Figure 8 for reaction 1 and Figure 9 for reaction 2. In both figures the steps are labeled so as to correspond to each other.

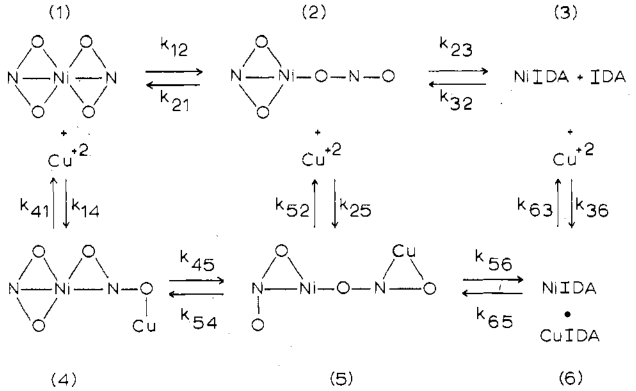


Figure 8. Proposed stepwise mechanism for the exchange of IDA between NiIDA and Cu. Protons are omitted for the sake of clarity.

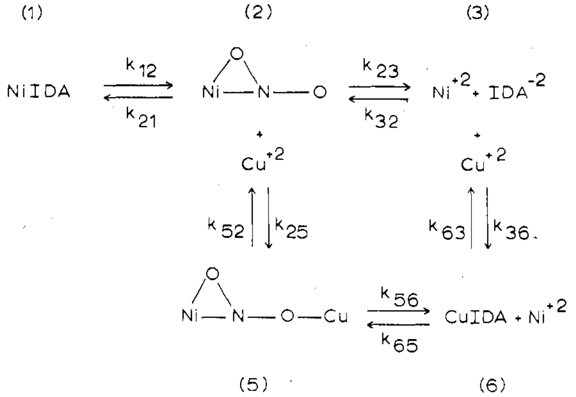


Figure 9. Proposed stepwise mechanism for the exchange of IDA between Ni and Cu. Protons are omitted for the sake of clarity.

For reaction 2, the pathway 1–2–3–6 of Figure 9 represents $k^{\mathrm{NiIDA}}{}_{\mathrm{H}}$ and k^{NiIDA} with the rate-determining step being the nickel–nitrogen bond breakage of step 2–3. The pathway 1–2–5–6, proceeding through the dinuclear intermediate, was found to hold at all copper concentrations studied. A general kinetic expression for this pathway, shown in eq 12, can be written by assuming the steady-state approximation for species 2 and 5. On comparison of terms in the denominator of eq

$$k_{\mathrm{slow}} = \frac{k_{12}k_{25}k_{56}[\mathrm{Cu}^{2+}]}{k_{21}k_{56} + k_{21}k_{52} + k_{25}k_{56}[\mathrm{Cu}^{2+}]} \tag{12}$$

12, $k_{25}k_{56}[\mathrm{Cu}^{2+}] > k_{21}k_{56}$ because k_{25} is at least 10^4 greater than k_{21} due to the difference in rates of water loss between copper and nickel. However, $k_{21}k_{52}$ is larger than $k_{25}k_{56}[\mathrm{Cu}^{2+}]$ even at 10^{-2} M copper due to the rapid rate of Cu–acetate dissociation compared to the sluggish rate of Ni–ammonia dissociation. Thus eq 12 becomes

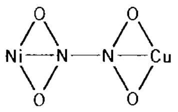
$$k_{\mathrm{slow}} = \frac{k_{12}k_{25}k_{56}[\mathrm{Cu}^{2+}]}{k_{21}k_{52}} \tag{13}$$

which shows the first-order dependence in copper that was found experimentally. Verification of eq 13 may be obtained by writing it as shown in eq 14 and predicting $k^{\mathrm{NiIDA}}{}_{\mathrm{Cu}}$ by using

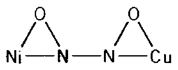
$$k_{\mathrm{slow}} = \frac{k_{12}k_{25}k_{56}[\mathrm{Cu}^{2+}]}{k_{21}k_{52}} = K_{\mathrm{r}}k_{56}[\mathrm{Cu}^{2+}] = k^{\mathrm{NiIDA}}{}_{\mathrm{Cu}}[\mathrm{Cu}^{2+}] \tag{14}$$

an accurate estimate of k_{56}. The value of K_{r} is 0.236 for species 5 and k_{56} may be obtained from the stability constant and rate of formation between nickel and glycine. Since the nickel–glycine formation reaction is thought to occur with nickel–nitrogen bond formation as the rate-determining step,[15] the

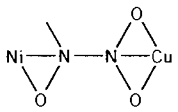
Table IV. Comparison of Ni(IDA)$_2$–Cu Structure I and NiL–Cu Reaction Intermediates[a]



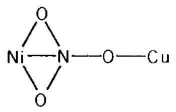
Ni(EDTA)Cu
$K_r = 1.50$



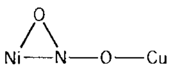
Ni(EDDA)Cu
$K_r = 1.91$



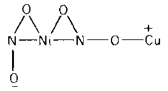
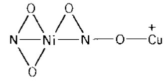
Ni(HEEDATA)Cu
$K_r = 0.179$



Ni(NTA)Cu
$K_r = 0.0222$



Ni(IDA)Cu
$K_r = 0.236$

structures to be tested	K_r	$K_r^{\mathrm{Ni(IDA)_2Cu}}/K_r^{\mathrm{Ni(EDTA)Cu}}$	$K_r^{\mathrm{Ni(IDA)_2Cu}}/K_r^{\mathrm{Ni(EDDA)Cu}}$	$K_r^{\mathrm{Ni(IDA)_2Cu}}/K_r^{\mathrm{Ni(HEEDTA)Cu}}$	$K_r^{\mathrm{Ni(IDA)_2Cu}}/K_r^{\mathrm{Ni(NTA)Cu}}$	$K_r^{\mathrm{Ni(IDA)_2Cu}}/K_r^{\mathrm{Ni(IDA)Cu}}$
Ia 	0.153	0.102 (0.021)	0.160[c] (0.030)	1.71[c] (0.069)	9.16[d] (0.034)	1.30[c] (0.052)
Ib 	33.9	60.6[b] (12.3)	94.9[b,c] (17.9)	1.01×10^{3} [b,c] (40.9)	5.44×10^{3} [b,d] (20.5)	766[b,c] (30.6)
$k'^{\mathrm{Ni(IDA)_2}}{}_{\mathrm{Cu}}/k^{\mathrm{NiL}}{}_{\mathrm{Cu}}$		4.93	5.29	24.7	266	25

[a] K_r values are based on the stability constants given in part II of Table III. The experimental ratios of rate constants are based upon the rate constant ratios given in part II of Table III. Statistical and electrostatic factors follow those of ref 10. Values in parentheses represent the ratio between the predicted relative stability constant ratio and the experimental rate constant ratio. [b] $K_{el} = 2.68$. [c] Statistical ratio of 2. [d] Statistical ratio of 1.33.

dissociation of the dinuclear intermediate with one acetate arm blocked by copper should be much like the dissociation of nickel glycine. A value of 6.7×10^{-2} s^{-1} is obtained for k_{56} with $K_{\mathrm{Ni(glycine)}} = 6.03 \times 10^{5}$[11] and $k^{\mathrm{Ni}}{}_{\mathrm{glycine}} = 2.2 \times 10^{4}$,[16] and this gives a predicted value of $k^{\mathrm{NiIDA}}{}_{\mathrm{Cu}} = 1.6 \times 10^{-2}$ M^{-1} s^{-1} which is in excellent agreement with the experimental values of 1.48×10^{-2} M^{-1} s^{-1}.

For reaction 1, the pathway 1–2–3–6 representing complete dissociation of IDA prior to copper attack is neglible in comparison to other pathways. A plot of k_{fast} vs. hydrogen concentration at a low constant copper concentration where no shift in order has yet occurred gives a zero slope. Further, plots of k_{fast} vs. copper concentration, such as shown in Figure 4, extrapolate to a zero intercept. Thus a complete dissociative pathway is kinetically unimportant.

Analogous to the NiEDDA–Cu and NiEDTA–Cu systems, reaction 1 proceeds through two pathways. At low copper concentration the reaction proceeds through the sequence 1–2–5–6 of Figure 8 with k_{56} as the rate-determining step. As the copper concentration increases, the relative concentration of species 5 increases and the rate at which species 2 is formed becomes rate limiting. A shift to a zero-order behavior in copper occurs with k_{12} as the rate-determining step. This never fully materializes, however, and a second first-order copper dependency, sequence 1–4–5–6, becomes predominant at high copper concentration. On the assumption of a steady state in species 2 and 5 and with $k_{41} > k_{45}$ such that species 4 can be assumed to be in rapid equilibrium with species 1, the following general equation can be derived.[1d,4]

$$k_{\text{fast}} = \{k_{12}k_{25} + k_{45}K_{41}(k_{21} + k_{25}[\mathrm{Cu}^{2+}])\}k_{56}[\mathrm{Cu}^{2+}]/\{k_{21}(k_{56} + k_{54} + k_{52}) + k_{25}(k_{56} + k_{54})[\mathrm{Cu}^{2+}]\}(1 + K_{41}[\mathrm{Cu}^{2+}]) \qquad (15)$$

At low copper concentration, under 0.01 M, $1 > K_{41}[\mathrm{Cu}^{2+}]$ because K_{41} will be similar in size to the values found for the NiEDTA–Cu system of 6.8[4] and certainly will not be larger than 10. Also following the NiEDDA–Cu and NiEDTA–Cu systems, where the same type of bonds are being broken and formed as in the present study, $k_{52} > (k_{54} + k_{56})$ and $k_{56} > k_{54}$. Finally, $k_{25}[\mathrm{Cu}] > k_{21}$ for the range of [Cu] used in this study, and $k_{12}k_{25} > k_{45}K_{41}k_{25}[\mathrm{Cu}^{2+}]$ because both k_{12} and k_{45} involve nickel dissociation and $K_{41}[\mathrm{Cu}^{2+}]$ is <1. Thus, eq 15 reduces to

$$k_{\text{fast}} = \frac{k_{12}k_{25}k_{56}[\mathrm{Cu}^{2+}]}{k_{21}k_{52} + k_{25}k_{56}[\mathrm{Cu}^{2+}]} \qquad (16)$$

which can be rearranged to

$$\frac{[\mathrm{Cu}^{2+}]}{k_{\text{fast}}} = \frac{k_{21}k_{52}}{k_{12}k_{25}k_{56}} + \frac{[\mathrm{Cu}^{2+}]}{k_{12}} \qquad (17)$$

Equation 17 has the same form as eq 9 which the experimental data follow as shown in Figure 6. At low copper concentration, $k_{21}k_{52} > k_{25}k_{56}[\mathrm{Cu}^{2+}]$ and eq 16 becomes

$$k_{\text{fast}} = \frac{k_{12}k_{25}k_{56}[\mathrm{Cu}^{2+}]}{k_{21}k_{52}} = k^{\mathrm{Ni(IDA)_2}}{}_{\mathrm{Cu}}[\mathrm{Cu}^{2+}] \qquad (18)$$

which is the rate constant for the low copper concentration first-order dependence. Step 5–6 is the rate-determining step. As the copper concentration increases, $k_{25}k_{56}[\mathrm{Cu}^{2+}]$ becomes large and a shift toward

$$k_{\text{fast}} = k_{12} \qquad (19)$$

is seen. The value of k_{52} is governed by copper–glycine dissociation for $\mathrm{Ni(IDA)_2}^{2-}$ and by copper–acetate for NiIDA.

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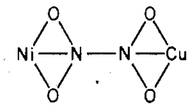
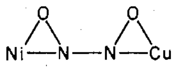
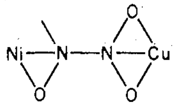
(15) D. W. Margerum, G. C. Cayley, D. C. Weatherburn, and G. K. Pagenkopf, *ACS Monogr.*, **No. 174**, 33 (1978).

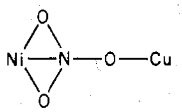
(16) J. C. Cassatt and R. G. Wilkins, *J. Am. Chem. Soc.*, **90**, 6045 (1968).

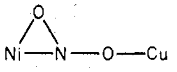
Table V. Comparison of $Ni(IDA)_2$-Cu Structure II and NiL-Cu Reaction Intermediates[a]

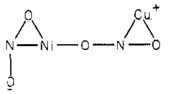
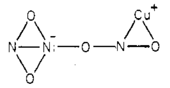

Ni(EDTA)Cu
$K_r = 1.50$


Ni(EDDA)Cu
$K_r = 1.91$


Ni(HEEDTA)Cu
$K_r = 0.179$


Ni(NTA)Cu
$K_r = 0.0222$


Ni(IDA)Cu
$K_r = 0.236$

structures to be tested		K_r	$K_r^{Ni(IDA)_2Cu}/K_r^{Ni(EDTA)Cu}$	$K_r^{Ni(IDA)_2Cu}/K_r^{Ni(EDDA)Cu}$	$K_r^{Ni(IDA)_2Cu}/K_r^{Ni(HEEDTA)Cu}$	$K_r^{Ni(IDA)_2Cu}/K_r^{Ni(NTA)Cu}$	$K_r^{Ni(IDA)_2Cu}/K_r^{Ni(IDA)Cu}$
IIa		3.74	2.07×10^3 [b,c] (15.4)	3.26×10^3 [b-d] (22.6)	3.48×10^4 [b-d] (51.8)	1.86×10^5 [b,c,e] (25.7)	2.63×10^4 [b-d] (38.7)
IIb		831	1.84×10^6 [b,f] (1.37×10^4)	2.88×10^6 [b,d,f] (2.00×10^4)	3.08×10^7 [b,d,f] (4.59×10^4)	1.65×10^8 [b,e,f] (2.28×10^4)	2.33×10^7 [b,d,f] (3.43×10^4)
$k^{Ni(IDA)_2}{}_{Cu}/k^{NiL}{}_{Cu}$			134	144	671	7240	680

[a] K_r values are based on the stability constants given in part II, Table III. The experimental ratios of rate constants are based upon the rate constant ratios given in part II, Table III. Stastical and electrostatic factors follow those of ref 10. Values in parentheses represent the ratio between the predicted relative stability constant ratio and the experimental rate constant ratio. [b] $k^{NiOAC}/k^{NiNH_3} = 830$. [c] $K_{el} = 2.89$. [d] Statistical ratio of 2. [e] Statistical ratio of 1.33. [f] $K_{el} = 3.98$.

Thus $k_{21}k_{52}$ is smaller for $Ni(IDA)_2^{2-}$, and an increase in copper concentration causes $k_{25}k_{56}[Cu^{2+}]$ to exceed $k_{21}k_{52}$.

The value of k_{12} is proton dependent as shown in Figure 7 and as described by eq 10. The value of $k^{Ni(IDA)_2}$, resolved from $k_{diss}^{Ni(IDA)_2}$, can be used to predict the structure of species 2 in Figure 8 much in the same fashion as was done for the structure of species 4 and 5. Equation 20[1d,4] can be used to

$$k_{12} = k_{21}\frac{K_{NiIDA}K_{Ni(acetate)}}{K_{Ni(IDA)_2}} \times \frac{1}{4} \times K_{el} \qquad (20)$$

predict $k^{Ni(IDA)_2}$ from a knowledge of the appropriate stability constants and the rate of water loss of NiIDA.[17] The term $K_{el} = 1.96$ represents electrostatic attraction of the uncoordinated acetate arm for nickel[10] and the factor of $^1/_4$ is a statistical factor that favors the dissociation of $Ni(IDA)_2^{2-}$. Equation 20 predicts a value of 0.184 s^{-1} which is 27 times larger than the experimental value of 6.85×10^{-3} s^{-1}. It is interesting to note that, again, the predicted value is high compared to the experimental value by the same amount as was found for the dinuclear intermediate structures of $Ni(IDA)_2^{2-}$.

At higher copper concentrations, above 0.01 M, a second first-order behavior appears and is attributed to the formation of species 4 of Figure 8. Similar structures have been found in the NiEDDA-Cu,[1d] NiEDTA-Cu,[4] CdCyDTA-Cu,[9] and CdCyDTA-Pb[9] systems. The slope of the plot shown in Figure 5 above 0.01 M copper can be used to calculate the rate constant for the formation of species 4, $k^{Ni(IDA)_2}{}_{Cu}$. The linearity of Figure 5 above 0.01 M copper shows that essentially just the sequence 1-4-5-6 is involved. By use of the steady-state approximation for species 5 and the assumption $[4] = K_{41}[Cu^{2+}]$ and with $k_{56} > k_{54}$, eq 21 results. The slope of Figure 5 above 0.01 M copper is 0.368 M^{-1} s^{-1}.

$$k_{fast} = K_{41}k_{45}[Cu^{2+}] \qquad (21)$$

The general mechanism of eq 15 can be simplified at high copper concentration. Again, $k_{52} > k_{56} + k_{54}$ and $k_{56} > k_{54}$ and following the NiEDDA-Cu system, $[Cu^{2+}] > k_{21}/k_{25}$ and $1 > K_{41}[Cu^{2+}]$. Thus eq 15 rearranges to

$$k_{fast}\left(\frac{k_{12} + k^{Ni(IDA)_2}{}_{Cu}[Cu^{2+}]}{k_{12}k^{Ni(IDA)_2}{}_{Cu}[Cu^{2+}]}\right) = 1 + \frac{k_{45}}{k_{12}}K_{41}[Cu^{2+}] \qquad (22)$$

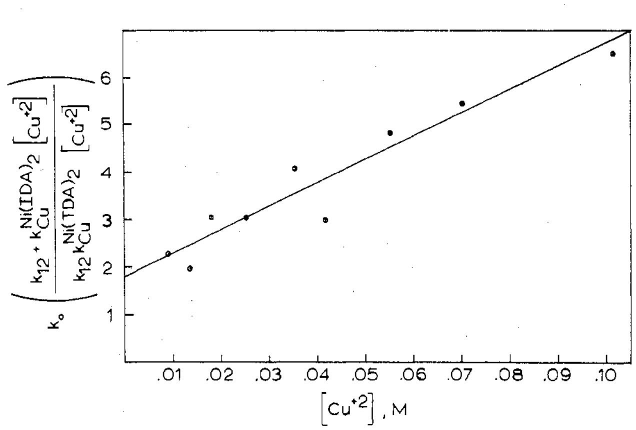


Figure 10. Plot of eq 22 showing adherence of experimental data to the general mechanism at high copper concentration at pH 3.8.

A plot of eq 22, shown in Figure 10, has an intercept of 1.8 and a slope yielding a value of $k_{45}K_{41} = 0.337$ M^{-1} s^{-1}. Thus the data fit eq 22 and the slope is in excellent agreement with the experimental value of $k_{45}K_{41}$ obtained from Figure 5.

The proposed general mechanism is seen to be in agreement with the experimental data over the whole range of copper concentrations studied. Further, the intermediate structures agree well with the experimental data provided a factor of about 30 is included for the effect of the coordinated IDA.

The Effect of Coordinated IDA. The exchange of IDA from $Ni(IDA)_2$ to copper proceeds by a factor of about 30 slower than expected. This must be due to the coordinated IDA decreasing nickel-ligand bond cleavage or accelerating nickel rate of water loss since the stability of the intermediate relative to the reactant is equal to the ratio of bond dissociation to bond formation.

The factor of 30 is not seen in the reaction of copper with NiIDA, reaction 2, yet reaction 2 yields the same dinuclear intermediate as reaction 1 at high copper concentration. Identical bonds are broken and formed in these two processes. The effect of the coordinated IDA enters the exchange mechanism prior to copper attack because the same factor is seen in the agreement between the predicted and experimental k_{12} values for the partial unwrapping of IDA from $Ni(IDA)_2$. Since the intermediate formed at high copper concentration involves only nickel-acetate dissociation and since the effect of the coordinated IDA is seen prior to copper attack, either the rate of dissociation of the nickel-acetate bond is decreased

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[17] J. P. Jones, E. J. Billo, and D. W. Margerum, *J. Am. Chem. Soc.*, **92**, 1875 (1970).

or the rate of water loss of the complex, upon which nickel–acetate formation is dependent, is accelerated. There is evidence to indicate that coordinated ligands do affect rate of water loss from complexes;[2] in fact, glycine[18] and IDA[17] have been shown to accelerate it. Indeed, the rate of water loss of $\text{NiIDA(H}_2\text{O)}_3$ was used in predicting k_{12}. However, the present system is more complex than this since two ligands are actually complexed to the nickel. Any effect that the IDA undergoing exchange has upon its own bond dissociation and formation is canceled out in the ratio of dissociation to formation rate constants, but the presence of synergistic effects is completely unknown. Thus, not enough information is available to allow identification of the exact effect of the coordinated IDA.

Comparison to Other Ni(ligand)–Cu Exchange Reactions. In comparison of Ni(ligand)–Cu metal exchange reactions, all are found to proceed through a dinuclear intermediate where sterically permitted. Only some, however, show a shift in order with respect to copper. The copper exchanges with NiEDDA, NiEDTA^{2-}, and $\text{Ni(IDA)}_2{}^{2-}$ all have order shifts while the copper exchanges with NiBPEDA^{2+} and NiIDA do not. Insufficient data were obtained during the copper-exchange reactions with NiNTA^{-}[19] and Ni(trien)^{2+} to allow any evaluation of order shift. The shift in order occurs because the relative concentration of the dinuclear intermediate increases as the copper concentration increases. In the present study, this is species 5, the steady-state approximation for which is[4]

$$\frac{[5]}{[2]} = \frac{k_{25}[\text{Cu}^{2+}]}{k_{56} + k_{52}} \tag{23}$$

As the copper concentration increases, the rate of formation of species 2, which does not depend on the copper concentration, becomes rate limiting.

Equation 23 provides the key to understanding why certain exchange systems show this order shift. In the reaction of copper with NiEDDA, NiEDTA^{2-}, NiBPEDA^{2+}, and NiIDA, k_{25} and k_{56} are the same, copper rate of water loss and nickel–nitrogen bond dissociation, respectively. Thus the value of k_{52} is important in determining the relative size of [5]. The structure of the dinuclear intermediate actually determines the value of k_{52} since the extent of unwrapping and subsequent coordination to copper determines what segment must dissociate from copper in step 5–2. Those dinuclear intermediates either where very little of the ligand has unwrapped or where the copper does not fully bond to the unwrapped segment will have large values of approximately 10^6 and $10^4\ \text{s}^{-1}$, respectively.[20] When a larger portion of the ligand has unwrapped, smaller values of k_{52} result. The NiEDDA and NiEDTA^{2-} systems represent this class and have k_{52} values of approximately 10 and $10^{-3}\ \text{s}^{-1}$, respectively. Thus the relative concentration of [5] will be considerably larger for NiEDDA and NiEDTA^{2-} than for NiIDA and NiBPEDA^{2+}. Since k_{12} is roughly the same for all four systems, an increase in copper concentration can cause $[5]k_{56}$ to exceed k_{12}, thus making k_{12} rate limiting.

In the Ni(IDA)_2–Cu system, 5–6 is no longer nickel–nitrogen bond breakage as is true for all the above systems. A comparison of $\text{Ni(IDA)}_2{}^{2-}$ to NiIDA shows why the order shift is seen for $\text{Ni(IDA)}_2{}^{2-}$. The denominator of eq 23 will be governed by whichever of the two terms predominates for each system. The value of k_{25} is the same for both systems. For $\text{Ni(IDA)}_2{}^{2-}$, k_{56}, nickel–acetate dissociation, is larger than k_{52}, copper–glycine dissociation, and is $5 \times 10^3\ \text{s}^{-1}$.[13] For NiIDA, k_{52}, copper–acetate dissociation, is larger than k_{56}, nickel–glycine dissociation, and is about $10^6\ \text{s}^{-1}$. Thus, the relative concentration of species 5 is about 10^3 larger for $\text{Ni(IDA)}_2{}^{2-}$ than for NiIDA. Further, k_{12} for $\text{Ni(IDA)}_2{}^{2-}$ is $5 \times 10^{-4}\ \text{s}^{-1}$ whereas the corresponding step for NiIDA is nickel–acetate bond dissociation which has a value of $5 \times 10^3\ \text{s}^{-1}$.[13] Thus the value of k_{12} can easily be exceeded for $\text{Ni(IDA)}_2{}^{2-}$ but for NiIDA, due to the large size of k_{12} and the correspondingly small relative value of [5], it would be virtually impossible to exceed k_{12} by merely changing the copper concentration.

The general conclusion that can be drawn is that systems where the dinuclear intermediate occurs early in the unwrapping process with correspondingly large values of k_{12} and large values of k_{52} will not show an order shift as the concentration of attacking metal is increased. The same conclusion can be reached if the attacking metal does not fully bond to the unwrapped ligand since this will cause k_{52} to be large despite the fact that k_{12} may be small. However, if large portions of the ligand unwrap and bond to the attacking metal prior to the rate-determining step, a shift in order with respect to the attacking metal can be expected.

Registry No. $\text{Ni(IDA)}_2{}^{2-}$, 23314-44-5; Cu^{2+}, 15158-11-9; Ni(IDA), 13869-33-5; $\text{Ni(ClO}_4\text{)}_2$, 13637-71-3; $\text{Cu(ClO}_4\text{)}_2$, 13770-18-8; $\text{Cu(IDA)}_2{}^{2-}$, 29826-48-0; Cu(IDA), 14219-31-9.

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(20) The k_{52} values are approximated from the rate of water loss of copper, $3 \times 10^8\ \text{s}^{-1}$, and the stability constant of the ligand segment bonded to copper. No attempt was made to calculate K_{os} values because order of magnitude values were all that were needed.