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Substituent Effects in Metal-Exchange Reactions. 1. Exchange Reaction between (Ethylenediamine-*N*,*N'*-di-α-propionato)nickel(II) and Copper(II)

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The reaction between copper(II) and (ethylenediamine-*N*,*N'*-di-α-propionato)nickel(II) was studied between pH 2.96 and 5.14 over a 25-fold variation in copper concentration at an ionic strength of 1.25 M and a temperature of 25 °C. Terms involving proton attack, copper attack, and copper hydroxide attack on the nickel complex as well as a pH- and copper-independent dissociation of the complex were resolved from the data. No order shift in copper concentration was seen as copper concentration was increased. The rate of copper attack on NiEDDP is a factor of 10 slower than that on NiEDDA. The presence of the α-methyl groups in EDDP results in the formation of a less stable dinuclear intermediate compared to the NiEDDA–Cu system. These groups also cause a more rapid unwrapping of EDDP compared to EDDA. Both of those effects are causes for the lack of an order shift in copper concentration. The rate of attack of $CuOH^+$ on NiEDDP is almost 2 orders of magnitude greater than that for other nickel polyaminocarboxylate systems. The NiEDDP–Cu dinuclear intermediate has an uncoordinated acetate arm on the nickel end of the species. It is proposed that a strong hydrogen bond forms between $CuOH^+$ and the free carboxylate group, which explains the very large increase in rate seen in comparing $k^{NiL}{}_{CuOH}$ to $k^{NiL}{}_{Cu}$.

Introduction

Although many factors can affect metal-exchange reactions,[1] the steric effect that a noncoordinating substituent placed between or on dentate sites of a multidentate ligand can have on a metal-exchange reaction has received little attention. Substituents can interfere with the ligand unwrapping and the dinuclear intermediate formation as well as alter the stability of the complexes. Only two studies have been carried out on substituent effects, both involving substituents on the ethylene backbone of the ligand. One study involved a cyclohexane ring on the ethylenediamine backbone of EDTA.[2] This ligand showed such a large steric effect that, for some metal pairs, no dinuclear intermediate formed and, for others, a very weakly bonded, distorted dinuclear intermediate formed outside the coordination cage. The other system involved a series of Schiff base ligands which formed two six-membered rings with the metal.[3] Square-planar geometry was forced on the complex, and no dinuclear intermediate was postulated.

The present study is concerned with the metal-exchange reaction between (ethylenediamine-*N*,*N'*-di-α-propionato)nickel(II) (NiEDDP) and copper(II) as represented by eq 1.

$$\mathrm{NiEDDP} + \mathrm{Cu}^{2+} \rightarrow \mathrm{CuEDDP} + \mathrm{Ni}^{2+} \qquad (1)$$

The ligand EDDP has a methyl group on the α-carbon of each acetate arm, thus creating a potential steric effect as EDDP unwraps from nickel and transfers to copper. Further, the α-methyl groups affect the initial stability of the complex as can be seen by comparing the stability constant of NiEDDA ($\log K = 13.65$) to that for NiEDDP ($\log K = 12.2$).[4] Comparison of the results obtained in this study with the structurally similar NiEDDA–copper system[5] shows the mechanism of the exchange reaction to be affected by the presence of the α-methyl substituents.

Experimental Section

Reagents. EDDP was prepared following the procedure of Schoenburg et al.[6] from *dl*-α-alanine and 1,2-dibromoethane. The white solid was recrystallized by dissolving it in aqueous base, adding acid to pH 5, and concentrating the solution by heat until crystals appeared. After cooling, the product was isolated. The melting point was 271.5 °C, which agrees with that found by Frausto Da Silva et al. of 278–280 °C[7] but not with that found by Schoenburg of 256–259 °C or Irving of 260–265 °C.[8] Anal. Calcd for $C_8H_{16}N_2O_4$: C, 47.06; H, 7.84; N, 13.73; O, 31.37. Found: C, 47.20; H, 8.15; N, 13.71; O, 31.77. An aqueous solution was titrated potentiometrically with standard base to yield a molecular weight of 204, which compared well with the theoretical value of 204.

Solutions of $Cu(ClO_4)_2$ and $Ni(ClO_4)_2$ were prepared from G. F. Smith metal salt hexahydrates and standardized by titration with EDTA. EDDP was standardized from a mole ratio plot with use of standard $Cu(ClO_4)_2$. NiEDDP was prepared by adding a 5% molar excess of $Ni(ClO_4)_2$ to a solution of EDDP followed by the addition of base to pH 10.5. The excess metal hydroxide was filtered and the pH of the solution adjusted to 7.0. The NiEDDP solution was standardized spectrophotometrically.

All other chemicals were reagent grade and were used without further purification. All solutions were prepared with deionized, distilled water. The ionic strength was maintained constant with $NaClO_4$.

Equilibrium and Kinetic Measurements. All pH measurements were made on a Beckman Model 110 research pH meter with a saturated NaCl reference electrode. Equilibrium spectrophotometric measurements were made on a Cary Model 14 spectrophotometer, and kinetic measurements were made on a Gilford Model 2000 spectrophotometer using a Beckman DU monochromator.

A spectral study of reactants and products showed the greatest change in molar absorptivity between reactants and products to be at 665 nm. All kinetic measurements were made at this wavelength. The molar absorptivities of reactants and products at 665 nm, μ = 1.25 M, are as follows: $Ni(ClO_4)_2$, 2.14; $Cu(ClO_4)_2$, 4.41; NiEDDP, 3.67; CuEDDP, 127.

The rate of reaction 1 was studied by following the increase in absorbance due to the formation of CuEDDP. No buffer was used since there was no net change in the number of protons in the reaction. This was demonstrated by mixing reactants and monitoring pH as the reaction proceeded. The copper concentration was varied from 1.9×10^{-3} to 4.9×10^{-2} M and was always in at least a 10-fold excess compared to NiEDDP concentration. The reaction was studied over a pH range of 2.96–5.14. All data were obtained at 25 ± 0.1 °C and μ = 1.25 M.

Results

The reaction of NiEDDP with copper was found to obey the first-order rate equation

$$\frac{-\mathrm{d}[\mathrm{NiEDDP}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{CuEDDP}]}{\mathrm{d}t} = k_0[\mathrm{NiEDDP}] \qquad (2)$$

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[1] (a) R. K. Steinhaus and S. H. Erickson, *Inorg. Chem.*, **19**, 1913 (1980). (b) E. Mentasti and E. Pelizzetti, *ibid.*, **17**, 3133 (1978). (c) D. W. Margerum, G. C. Cayley, D. C. Weatherburn, and G. K. Pagenkopf, *ACS Monogr.*, **No. 174**, 163 (1978).

[2] G. A. Nyssen and D. W. Margerum, *Inorg. Chem.*, **9**, 1814 (1970).

[3] G. Kohler and H. Elias, *Inorg. Chim. Acta*, **34**, L215 (1979).

[4] A. E. Martell and R. M. Smith, "Critical Stability Constants", Vols. 1 and 2, Plenum Press, New York, 1974.

[5] R. K. Steinhaus and R. L. Swann, *Inorg. Chem.*, **12**, 1855 (1973).

[6] L. H. Schoenburg, D. W. Cooke, and C. F. Liu, *Inorg. Chem.*, **7**, 2386 (1968).

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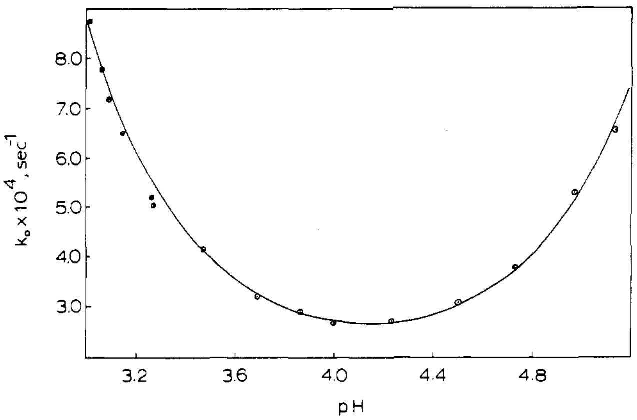

Figure 1. Dependence of k_0 upon pH for the reaction of NiEDDP with copper: $\mu = 1.25$ M, $T = 25$ °C. The copper concentration is constant at 1.96×10^{-2} M. The solid line is the curve predicted from eq 4; circled points are experimentally observed values.

Table I. Variation of the Observed First-Order Rate Constants for Eq 1 with Respect to pH and Excess Copper Ion Concentration ($\mu = 1.25$ M, $T = 25$ °C)[a]

pH	$10^2[\mathrm{Cu}^{2+}]$, M	10^4k, s^{-1}	pH	$10^2[\mathrm{Cu}^{2+}]$, M	10^4k, s^{-1}
2.961	1.96	9.36	3.986	4.73	5.21
2.987	1.96	8.67	4.230	0.946	1.61
3.014	1.96	8.73	4.228	1.42	2.14
3.062	1.96	7.78	4.231	1.89	2.70
3.091	1.96	7.18	4.228	2.36	3.16
3.147	1.96	6.50	4.222	2.84	3.67
3.260	1.96	5.20	4.231	3.92	4.45
3.272	1.96	5.03	4.240	4.90	5.93
3.469	1.96	4.15	4.507	1.96	3.06
3.698	1.96	3.19	4.799	0.473	1.28
3.865	1.96	2.88	4.725	0.946	2.25
3.994[b]	0.190	0.882	4.712	1.42	3.44
3.979[c]	0.285	0.936	4.736	1.42	3.36
3.983[c]	0.380	1.16	4.750	1.47	3.08
3.996	0.473	1.22	4.725	1.89	4.27
4.012	0.946	1.58	4.734	1.96	3.80
3.988	1.42	2.09	4.702	2.36	4.48
4.029	1.47	2.38	4.703	2.84	5.43
3.998	1.89	2.67	4.708	3.78	6.91
3.982	2.36	2.92	4.720	3.78	6.11
3.996	2.45	3.34	4.970	1.96	5.30
3.993	2.84	3.47	5.136	1.96	6.58
3.986	3.78	3.72			

[a] [NiEDDP] = 4.45×10^{-4} M in all runs except as noted. [b] [NiEDDP] = 1.79×10^{-4} M. [c] [NiEDDP] = 2.24×10^{-4} M.

where k_0 represents the pseudo-first-order rate constant. Excellent first-order plots were obtained covering 3 half-lives. After the kinetic behavior was well established, a curve-fitting program was used for each run to obtain optimum values of the observed pseudo-first-order rate constant, the final absorbance of the reaction, A_∞, and the change in absorbance that the reaction experienced, A_1. The program gave the best least-squares fit to eq 3. Very good agreement between the

$$A_t = A_1e^{-kt} + A_\infty \tag{3}$$

predicted and experimental absorbance values was found with the assumption that the reaction went to completion.

The effect of pH upon the rate is shown in Figure 1, which demonstrates that both hydrogen and hydroxide terms are present. Table I lists the data. Previous work on similar systems[1,5,9-11] has shown all of the following terms to contribute to the rate of metal-exchange reactions: proton attack, copper attack, and copper hydroxide attack on the nickel complex, as well as pH- and copper-independent dissociation of the nickel complex. Each of these terms may play a large or small role or be nonobservable in a given metal-exchange system depending upon the ligand and metal pair involved. A complete rate equation for the exchange is given in eq 4. With

Table II. Resolved Rate Constants for the Reaction of NiEDDP and Cu^{2+} ($\mu = 1.25$ M, $T = 25$ °C)

constant	value
$k^{\mathrm{NiL}}{}_{\mathrm{H}}$	$(7.09 \pm 0.19) \times 10^{-1}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$
$k^{\mathrm{NiL}}{}_{\mathrm{CuOH}}$	$9.66 \pm 0.48\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$
k^{NiL}	$(1.71 \pm 0.75) \times 10^{-5}\ \mathrm{s}^{-1}$
$k^{\mathrm{NiL}}{}_{\mathrm{Cu}}$	$(7.51 \pm 0.29) \times 10^{-3}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$

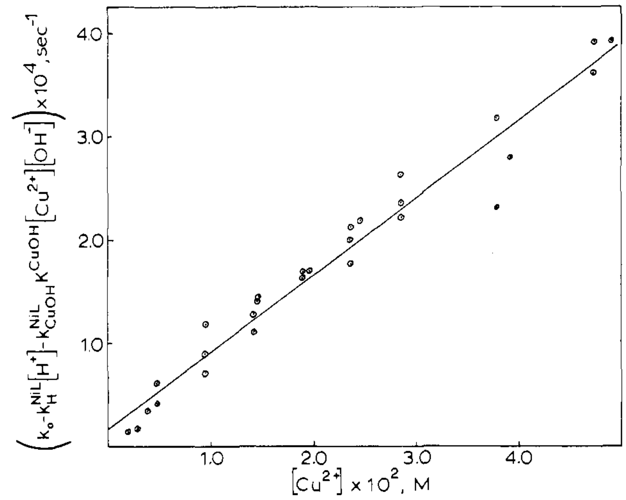

Figure 2. Resolution of $k^{\mathrm{NiL}}{}_{\mathrm{Cu}}$ and k^{NiL} using eq 6: $\mu = 1.25$ M, $T = 25$ °C.

$$\frac{-d[\mathrm{NiEDDP}]}{dt} = k_0[\mathrm{NiEDDP}] = (k^{\mathrm{NiL}} + k^{\mathrm{NiL}}{}_{\mathrm{H}}[\mathrm{H}^+] + k^{\mathrm{NiL}}{}_{\mathrm{Cu}}[\mathrm{Cu}^{2+}] + k^{\mathrm{NiL}}{}_{\mathrm{CuOH}}[\mathrm{CuOH}^+])[\mathrm{NiEDDP}] \tag{4}$$

the assumption of CuOH^+ to be the reactive species, as is the case with NiEDTA^{2-}[11] and $\mathrm{NiBPEDA}^{2+}$,[9] the last term in parentheses in eq 4 can be written as

$$k^{\mathrm{NiL}}{}_{\mathrm{CuOH}}K^{\mathrm{CuOH}}K_{\mathrm{w}}\frac{[\mathrm{Cu}^{2+}]}{[\mathrm{H}^+]}$$

with

$$K^{\mathrm{CuOH}} = \frac{[\mathrm{CuOH}^+]}{[\mathrm{Cu}^{2+}][\mathrm{OH}^-]} = 2.0 \times 10^{6}$$ [12]

At constant copper concentration, eq 4 becomes

$$k_0 = k_{\mathrm{I}} + k_{\mathrm{II}}\frac{1}{[\mathrm{H}^+]} + k^{\mathrm{NiL}}{}_{\mathrm{H}}[\mathrm{H}^+] \tag{5}$$

where $k_{\mathrm{I}} = k^{\mathrm{NiL}}{}_{\mathrm{Cu}}[\mathrm{Cu}^{2+}] + k^{\mathrm{NiL}}$ and $k_{\mathrm{II}} = k^{\mathrm{NiL}}{}_{\mathrm{CuOH}}K^{\mathrm{CuOH}}K_{\mathrm{w}}[\mathrm{Cu}^{2+}]$. Multiple linear regression analysis of equation 5 using kinetic data at constant copper concentration yielded $k^{\mathrm{NiL}}{}_{\mathrm{H}} = 0.709\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $k^{\mathrm{NiL}}{}_{\mathrm{CuOH}} = 9.66\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. Both values are listed in Table II.

For values of k^{NiL} and $k^{\mathrm{NiL}}{}_{\mathrm{Cu}}$, eq 4 was rewritten as shown in eq 6 and a plot of the left-hand side of eq 6 vs. copper

$$k_0 - k^{\mathrm{NiL}}{}_{\mathrm{H}}[\mathrm{H}^+] - k^{\mathrm{NiL}}{}_{\mathrm{CuOH}}K^{\mathrm{CuOH}}[\mathrm{Cu}^{2+}][\mathrm{OH}^-] = k^{\mathrm{NiL}} + k^{\mathrm{NiL}}{}_{\mathrm{Cu}}[\mathrm{Cu}^{2+}] \tag{6}$$

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(9) R. K. Steinhaus and C. L. Barsuhn, *Inorg. Chem.*, **13**, 2922 (1974).

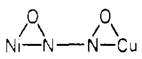
(10) D. W. Margerum, B. A. Zabin, and D. L. Janes, *Inorg. Chem.*, **5**, 250 (1966).

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

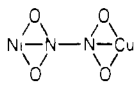
(12) A. E. Martell and R. M. Smith, "Critical Stability Constants", Vol. 4, Plenum Press, New York, 1974.

Table III. Comparison of NiEDDP-Cu and NiL-Cu Reaction Intermediates[a]

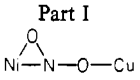
Part I



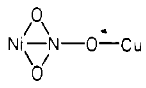
Ni(EDDA)Cu
$K_r = 1.91$



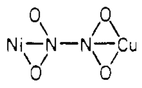
Ni(EDTA)Cu
$K_r = 1.50$



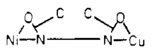
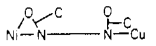
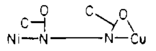
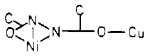
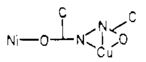
Ni(IDA)Cu
$K_r = 0.244$



Ni(NTA)Cu
$K_r = 0.022$



Ni(HEEDTA)Cu
$K_r = 0.18$

structures to be tested	K_r	$K_r^{\text{Ni(EDDP)Cu}}/K_r^{\text{Ni(EDDA)Cu}}$	$K_r^{\text{Ni(EDDP)Cu}}/K_r^{\text{Ni(EDTA)Cu}}$	$K_r^{\text{Ni(EDDP)Cu}}/K_r^{\text{Ni(IDA)Cu}}$	$K_r^{\text{Ni(EDDP)Cu}}/K_r^{\text{Ni(NTA)Cu}}$	$K_r^{\text{Ni(EDDP)Cu}}/K_r^{\text{Ni(HEEDTA)Cu}}$
I 	21.4	11.2	7.15[b]	90.7	643[c]	119
II 	3.16×10^{-3}	1.65×10^{-2} [d]	1.05×10^{-2} [b,d]	0.134[d]	0.946[c,d]	0.176[d]
III 	4.28×10^{-2}	0.224[d]	0.142[b,d]	1.81[d]	12.8[c,d]	0.239[d]
IV 	0.913	0.478	0.304[b]	3.87	27.4[c]	5.10
V 	87.3	3.79×10^{4} [e]	2.42×10^{4} [b,e]	3.06×10^{5} [e]	2.17×10^{6} [c,e]	4.04×10^{5} [e]
$k^{\text{NiEDDP}}{}_{\text{Cu}}/k^{\text{NiL}}{}_{\text{Cu}}$		0.100	0.469	0.507	5.40	0.500

Part II

complex	K_{stab}	M	$k^{\text{NiL}}{}_{\text{Cu}}$, M^{-1} s^{-1}
NiEDDP	1.58×10^{12}	Cu	7.51×10^{-3} [f]
NiEDDA	4.46×10^{13}	Cu	7.49×10^{-2} [g]
NiEDTA^{2-}	3.31×10^{18}	Cu	1.6×10^{-2} [h]
NiIDA	1.3×10^{8}	Cu	1.48×10^{-2} [i]
NiNTA^{-}	3.16×10^{11}	Cu	1.3×10^{-3} [j]
NiHEEDTA	1.25×10^{17}	Cu	1.5×10^{-2} [k]
Ni(alanine)^{+}	2.5×10^{5}		
Ni(acetate)^{+}	5.5		
$\text{NiNH}_3{}^{2+}$	5.0×10^{2}		
NiEDMA	2.75×10^{10}		
Cu(alanine)^{+}	1.35×10^{8}		
Cu(acetate)^{+}	5.25×10^{4}		
$\text{CuNH}_3{}^{2+}$	1.99×10^{4}		
CuEDMA	2.51×10^{13}		

[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, with μ = 1.25 M, T = 25 °C. All values were taken from ref 4. Statistical and electrostatic factors follow those of ref 13. [b] Statistical factor of $^1/_2$ included. [c] Statistical factor of $^2/_3$ included. [d] Electrostatic factor of 10. [e] $k^{\text{NiOAc}}/k^{\text{NiNH}_3} = 830$. [f] This work. [g] Reference 5. [h] Reference 11. [i] Reference 1a. [j] Reference 14. [k] Reference 13.

concentration was made as shown in Figure 2. Points are used covering the pH range 3.98–4.72. A least-squares fit of the data gives $k^{\text{NiL}} = 1.71 \times 10^{-5}$ s^{-1} and $k^{\text{NiL}}{}_{\text{Cu}} = 7.51 \times 10^{-3}$ M^{-1} s^{-1}. These values are also listed in Table II. The fact that all the points covering a range of pH values and copper concentrations fit the same line as shown in Figure 2 is good indication that no other kinetically active terms are present. Finally, the four resolved rate constants were used in eq 4 to construct the solid line of Figure 1. The excellent agreement seen between the observed and predicted data is further proof that the resolved terms are correct.

Discussion

The NiEDDP–Cu system appears to proceed through three different pathways: (1) a complete dissociation of NiEDDP followed by attack of copper on dissociated EDDP, the pathway represented by k^{NiL}; (2) a proton-assisted dissociation of NiEDDP followed by attack of copper, the pathway represented by $k^{\text{NiL}}{}_{\text{H}}$; (3) an attack by both copper and CuOH$^+$ on partially dissociated NiEDDP to yield a dinuclear intermediate, the pathway represented by $k^{\text{NiL}}{}_{\text{Cu}}$ and $k^{\text{NiL}}{}_{\text{CuOH}}$. Of interest is the lack of an order shift in the mechanism as a function of copper concentration such as that seen for the copper attack on NiEDTA^{2-},[11] NiEDDA,[5] and $\text{Ni(IDA)}_2{}^{2-}$.[1] However, lack of a shift to zero order in copper at high copper concentration coupled with a relatively low value for the copper attack on NiEDDP allows the CuOH$^+$ term to predominate at high pH, a feature not seen in the above system.

Structure of the Partially Unwrapped Intermediate. Previous studies of metal-exchange reactions have shown that these reactions proceed through a copper-dependent dinuclear intermediate unless sterically hindered. Further, the structure of the dinuclear intermediate immediately prior to the rate-determining step may be characterized by a comparison of rate constant ratios to relative stability constant ratios using similar systems as shown in eq 7. The comparison assumes the same

$$\frac{k^{\text{NiEDDP}}{}_{\text{Cu}}}{k^{\text{NiL}}{}_{\text{Cu}}} = \frac{K_r^{\text{Ni(EDDP)Cu}}}{K_r^{\text{Ni(L)Cu}}} \qquad (7)$$

rate-determining step to hold for both systems. The value of K_r is calculated according to eq 8. Table III lists the com-

$$K_r = \frac{K_{\text{Ni segment}} K_{\text{Cu segment}}}{K_{\text{Ni complex}}} \qquad (8)$$

parisons between the known structures and the five logical dinuclear intermediate structures for NiEDDP–Cu. Electrostatic and statistical factors are included where appropriate. A factor of 830[1,13] is used where needed to compensate for the

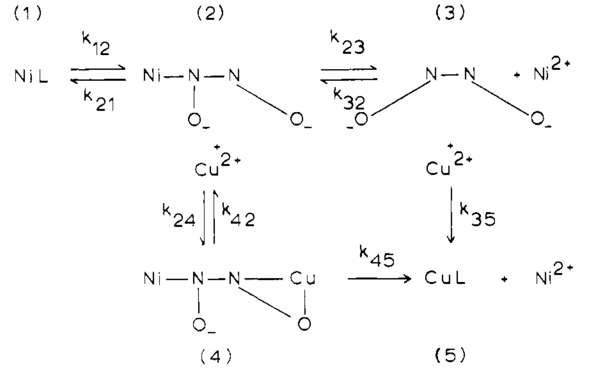


Figure 3. General mechanism for the transfer of EDDP from nickel to copper. Protons and carbon atoms have been omitted for simplicity. L represents EDDP.

difference between cleavage of a nickel–acetate bond compared to that of a nickel–nitrogen bond. Structure III gives the closest agreement between the experimental ratios and those predicted from eq 7 although structures II and IV give modest agreement in some cases.

Confirmation of structure III is obtained by calculating the rate of k^{NiEDDP} much in the same fashion as was done for the dinuclear intermediate. Equation 9 can be used to predict k^{NiL}

$$k^{\mathrm{NiL}} = k^{\mathrm{Ni(NH_3)-H_2O}}\frac{K^{\mathrm{NiNH_3}}}{K^{\mathrm{NiEDDP}}}{}^1\!/_2K_{\mathrm{el}} \tag{9}$$

from a knowledge of the appropriate stability constants and the rate of water loss of $\mathrm{Ni(NH_3)(H_2O)_5}^{2+}$. The factor of $^1/_2$ is a statistical factor that favors the dissociation of NiEDDP, and K_{el} represents electrostatic attraction between the uncoordinated acetate arm nearest nickel and nickel itself. Calculation of k^{NiL} for the partially unwrapped species of structure III in Table III, without copper present, yields a value of 3.2 × 10^{-5} s^{-1} whereas use of the partially unwrapped species of structure II of Table III yields a value of 0.030 s^{-1} and that of structure IV yields a value of 0.11 s^{-1}. The values of all three structures are to be compared to the experimental value of 1.71 × 10^{-5} s^{-1}. The latter two values, calculated from structures II and IV, are much too high as a result of having an alanine segment bonded to nickel in the case of structure II and of having only an acetate arm unwrapped in the case of structure IV. The value for structure III compares to the experimental value within a factor of 2 and confirms structure III as the dinuclear intermediate. The rate-determining step must be rupture of the remaining Ni–N bond.

General Mechanism. Knowledge of the structure of the dinuclear intermediate allows a mechanism to be postulated for the metal exchange of NiEDDP and copper. This is shown in Figure 3. The reaction pathway **1–2–3–5** represents k^{NiL} with k_{23} being the rate-determining step, and pathway **1–2–4–5** represents $k^{\mathrm{NiL}}{}_{\mathrm{H}}$, $k^{\mathrm{NiL}}{}_{\mathrm{Cu}}$, and $k^{\mathrm{NiL}}{}_{\mathrm{CuOH}}$, depending upon the attacking species. Rupture of the Ni–N bond in species **4** is the rate-determining step. A kinetic expression shown in eq 10 for pathway **1–2–3–5** may be written by assuming a steady

$$k^{\mathrm{NiL}} = \frac{k_{12}k_{23}}{k_{21} + k_{23}} \tag{10}$$

state for species **2** of Figure 3. Likewise, for pathway **1–2–4–5**, with either copper, $\mathrm{CuOH^+}$ or proton attack, and with the assumption of a steady state in species **2** and **4** of Figure 3, eq 11 results with X being copper, $\mathrm{CuOH^+}$, or $\mathrm{H^+}$. In a

$$k^{\mathrm{NiL}}{}_{\mathrm{X}} = \frac{k_{12}k_{24}k_{45}[\mathrm{X}]}{k_{21}k_{45} + k_{21}k_{42} + k_{24}k_{45}[\mathrm{X}]} \tag{11}$$

comparison of terms in the demoninator of eq 11, $k_{21}k_{42} > k_{21}k_{45}$ because of the rapid rate of water loss of copper (k_{42}) compared to the sluggish rate of Ni–N bond dissociation (k_{45}). Further, $k_{24}k_{45}[\mathrm{X}] > k_{21}k_{45}$ because k_{24}/k_{21} is at least 10^4 due to the difference in rates of water loss between copper and nickel and the fact that the concentration of X never becomes smaller than 10^{-3} M since the largest of the three, $\mathrm{Cu^{2+}}$, $\mathrm{CuOH^+}$, or $\mathrm{H^+}$, predominates kinetically, so that $k_{24}[\mathrm{X}] > k_{21}$. Thus, $k_{21}k_{42}$ predominates in the denominator such that eq 11 simplifies to eq 12, which shows the first-order dependence in copper, $\mathrm{CuOH^+}$, and $\mathrm{H^+}$ that was found experimentally.

$$k^{\mathrm{NiL}} = \frac{k_{12}k_{24}k_{45}[\mathrm{X}]}{k_{21}k_{42}} \tag{12}$$

Table IV. Comparison of Rate Constants for the Attack of $\mathrm{Cu^{2+}}$ and $\mathrm{CuOH^+}$ on Various Complexes[a]

complex	$k^{\mathrm{NiL}}{}_{\mathrm{Cu}}$	$k^{\mathrm{NiL}}{}_{\mathrm{CuOH}}$	$k^{\mathrm{NiL}}{}_{\mathrm{CuOH}}/k^{\mathrm{NiL}}{}_{\mathrm{Cu}}$
NiEDDP	7.51 × 10^{-3}	9.29	1240[b]
$\mathrm{NiBPEDA^{2+}}$	4.9 × 10^{-4}	0.108	220[c]
$\mathrm{Ni(trien)^{2+}}$	2.7	80	30[d]
$\mathrm{NiEDTA^{2-}}$	7.5 × 10^{-2}	1.4	18[e,f]
$\mathrm{ZnEDTA^{2-}}$	67	220	33[g]

[a] All rate constants in $\mathrm{M^{-1}\ s^{-1}}$ at 25 °C. [b] This work. [c] Reference 9. [d] Reference 15. [e] Reference 11. [f] The data to resolve $k^{\mathrm{NiEDTA}}{}_{\mathrm{Cu}}$ and $k^{\mathrm{NiEDTA}}{}_{\mathrm{CuOH}}$ were not corrected for any hydrolyzed copper species. [g] Reference 10.

Table V. Effect of Hydroxide on the Stability of Copper(II) Complexes

reacn	log K_{stab}
$\mathrm{Cu(en)_2}^{2+} + \mathrm{OH^-} \rightarrow \mathrm{Cu(en)_2OH^+}$	5.8[a]
$\mathrm{CuDMEN^{2+}} + \mathrm{OH^-} \rightarrow \mathrm{Cu(DMEN)OH^+}$	5.9[b]
$\mathrm{Cu(dien)^{2+}} + \mathrm{OH^-} \rightarrow \mathrm{Cu(dien)OH^-}$	5.0[c]
$\mathrm{CuHEEN^{2+}} + \mathrm{OH^-} \rightarrow \mathrm{Cu(HEEN)OH^+}$	6.7[c]
$\mathrm{Cu(trien)^{2+}} + \mathrm{OH^-} \rightarrow \mathrm{Cu(trien)OH^+}$	3.8[d]

[a] Reference 16. [b] Reference 17. [c] Reference 18. [d] Reference 19.

$\mathrm{CuOH^+}$ Attack. The rate constant for the attack of $\mathrm{CuOH^+}$ on NiEDDP shows enhanced behavior compared to that for copper as can be seen by comparing rate constants in Table II. The accelerating effect of hydrolyzed copper has been seen in other systems as shown in Table IV. It is interesting to note that, in the present system, the ratio of $k^{\mathrm{NiL}}{}_{\mathrm{CuOH}}/k^{\mathrm{NiL}}{}_{\mathrm{Cu}}$ is 1240 compared to 220 for the NiBPEDA system[9] and about 30 for the $\mathrm{Ni(trien)^{2+}}$,[15] $\mathrm{NiEDTA^{2-}}$,[11] and $\mathrm{ZnEDTA^{2-}}$[10] systems. The addition of $\mathrm{OH^-}$ to either $\mathrm{Cu(H_2O)_6}^{2+}$ or to copper complexes results in a gain in stability of about 6 log units as can be seen in Table V, which lists some systems pertinent to the present system. However, any gain in stability of the dinuclear intermediate resulting from the formation of an $\mathrm{Ni(EDDP)CuOH^+}$ species will be offset by using $\mathrm{CuOH^+}$ as a reactant because the former appears in the denominator of the K_{r} expression and the latter in the numerator. In fact, as can be seen in Table V, the increase in stability as a result of hydroxide formation experienced by a complex is less than the 10^6 gain in stability experienced by copper through the formation of $\mathrm{CuOH^+}$. Thus, K_{r} values using copper hydroxide stability constants would actually decrease and cannot be the

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explanation for the increase in rate seen experimentally.

The explanation that has been previously set forth is that the enhanced rate of attack of $CuOH^+$ is due to the formation of some type of hydrogen-bonded or hydroxide-bridged intermediate which imparts an added degree of stability to the intermediate. In the present system, the free acetate arm on the portion of ligand still bonded to nickel would be an excellent nucleophile, far stronger than anything that exists in any of the other systems. The strength of any type of hydrogen bond between the carboxyl group and the hydroxide bonded to copper would cause considerable increases in stability of the intermediate, which would be reflected in the $k^{\mathrm{NiL}}_{\mathrm{CuOH}}/k^{\mathrm{NiL}}_{\mathrm{Cu}}$ ratio. Thus, as the data show, the factor of 1240 increase would be unique to the ligand with a free acetate arm.

The effect of substituting a methyl group on each acetate arm, a seeminglessly inert substitution, has profound effects on the mechanism. A comparison of the stability constants of (ethylenediaminemonoacetato)nickel(II) (NiEDMA) and NiEDDP shows a gain of only 57 for EDDP, the ligand possessing an additional acetate arm with an α-methyl group.[4] If it is assumed that one of the acetate arms of EDDP is uncoordinated in the nickel complex, an electrostatic attraction of 3.16 would nevertheless exist such that the added acetate arm of EDDP contributes an increase of only about 20 to the stability of the NiEDDP complex compared to the case for NiEDMA. Thus, the addition of an α-methyl group on the acetate arms of EDDP results in a nickel complex with either two nitrogens and one acetate coordinated or the second acetate only very weakly bonded. As EDDP unwraps from nickel, only one nickel–nitrogen bond need rupture, followed by cleavage of the other acetate arm from nickel, in order to achieve structure **2** of Figure 3, the precursor of the dinuclear intermediate. This would cause k_{12} to be considerably faster for NiEDDP compared to that for NiEDDA, where all four dentate sites are strongly coordinated in the metal complex and where an entire glycine segment must dissociate to get to the dinuclear intermediate precursor.

This very weak coordination or lack of coordination of an acetate arm causes the stability of the nickel complex of EDDP to be lowered by a factor of 30 relative to that for NiEDDA.[4] The drop in stability of the initial complex and the lack of acetate coordination seen in the dinuclear intermediate lowers the stability of the dinuclear intermediate relative to that for NiEDDA–Cu. Hence, as eq 7 shows, the rate constant for the metal-exchange pathway is lower.

The two effects discussed above result in an interesting change in mechanism for the EDDP system compared to the EDDA system.[5] The NiEDDA–Cu system shows a shift in order with respect to copper as the copper concentration is increased, yet NiEDDP–Cu does not. In order for the shift in order with respect to copper to be seen, k_{45}[species **4**] must exceed the value of k_{12} as copper concentration increases. The concentration of species **4** depends upon the copper concentration as can be seen in Figure 3. Experimentally, no order shift was seen with the conclusion that k_{12} for NiEDDP is larger than that of NiEDDA or [species **4**] in the EDDP system is less than that of the EDDA system or both. As previously discussed, weak acetate coordination to nickel causes k_{12} for NiEDDP to be larger than that for NiEDDA. Further, the rate constant $k^{\mathrm{NiL}}_{\mathrm{Cu}}$ for either system can be written as k_{45}[species **4**]. It is reasonable to assume that the value of k_{45}, rupture of a nickel–nitrogen bond, is about the same for both systems. The experimental decrease of 10 seen in comparing $k^{\mathrm{NiL}}_{\mathrm{Cu}}$ for EDDP to that for EDDA can be attributed to a lower stability for the NiEDDP–Cu dinuclear intermediate and thus indicates that [species **4**] for EDDP compared to that for EDDA makes it impossible for k_{45}[species **4**] $> k_{12}$ for the EDDP system, resulting in first-order behavior in copper over the entire copper concentration range studied.

The interesting effect of the α-methyl substituents has prompted further studies involving other substituent groups on an EDDA base ligand, which are currently being carried out in our laboratories.

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Heteronuclear Ferrocene–Ruthenium Mixed-Valence Ions. Bi- and Trinuclear Species Based on the 1,1′-Dicyanoferrocene Ligand

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The heterotrimetallic ion $[(NH_3)_5RuNCFcCNRu(NH_3)_5](PF_6)_4$ as well as the corresponding heterobinuclear complex $[(NH_3)_5RuNCFcCN](PF_6)_2$ containing one less ruthenium center have been prepared from the 1,1′-dicyanoferrocenyl moiety. The similarity between the spectral and electrochemical properties of the mixed-valence species derived from both the trinuclear ion and its binuclear congener indicates the presence of weak electronic interaction between the ferrocene center and ruthenium nuclei in these complexes, with no evidence for end-to-end interaction in the monooxidized trinuclear species, $[(NH_3)_5Ru^{II}NCFcCNRu^{III}(NH_3)_5]^{5+}$. The unsymmetrical nature of the charge transfer in these ferrocene–ruthenium ions has been used to advantage to determine the effect of the electrostatic contribution to the intervalence transfer transition energies in these species. The absence of electronic interaction between the terminal ruthenium sites in the (2,2,3) ion allowed the correlation of the experimentally observed electrostatic stabilization for this species with the theoretically determined value, without recourse to estimating a value for a contribution due to ground-state stabilization. The result of this correlation is in keeping with the previous suggestion of an underestimation of the electrostatic contribution by the theoretical expression.

Introduction

Discrete mixed-valence complexes have now received significant attention in the literature since the initial theoretical work by Hush,[2] describing the properties of the related thermal and optical electron-transfer processes that occur in weakly coupled mixed-valence systems. A number of studies have

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