

Contribution from the Department of Chemistry,
Western Michigan University, Kalamazoo, Michigan 49001**Kinetics of the Metal-Exchange Reaction between
N,N'-Bis(2-picoly)ethylenediaminenickel(II) and Copper(II)**

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The kinetics of the metal-exchange reaction between *N,N'*-bis(2-picoly)ethylenediaminenickel(II) and copper(II) has been studied over the pH range of 3.7–6.0 at six different copper concentrations ranging from 4×10^{-3} to 2×10^{-2} M and at an ionic strength of 0.1 M and 25°. The reaction is first order in both NiBPEDA²⁺ and copper. The rate varies inversely with the first power of hydrogen ion at low pH and inversely with the second power at higher pH. This can be attributed to the attack of the Cu²⁺, CuOH⁺, and Cu₂(OH)₂²⁺ species on NiBPEDA²⁺. The exchange reaction at higher total copper and higher pH shows additional hydrolyzed copper species to be present although none of the species proposed in the literature fit the kinetic data. The exchange reaction is characterized as proceeding through a dinuclear intermediate having an aminoethylpyridine segment bonded to Ni and a free aliphatic nitrogen bonded to Cu. Comparisons to analogous metal-exchange reactions are made and are used to find the most likely explanation for the increased reactivity of CuOH⁺ and Cu₂(OH)₂²⁺.

Introduction

Metal-exchange reactions of multidentate ligand complexes, represented by eq 1, have been the subject of very exten-



sive study.¹ Previous papers have dealt with the characteristics of these reactions as well as the type of information which may be gained from them.

Most of the systems studied thus far have involved amino-carboxylate ligands, whereas only two reports of metal-exchange reactions involving polyamine ligands have appeared.^{2,3} None of these have dealt with the interesting class of polyamines having both aliphatic and aromatic dentate sites. These ligands are unusual in that the aromatic nitrogens are relatively quite acidic yet without a corresponding decrease in metal stability.^{4,5} Thus, compared to complexes of the aliphatic analogs, their complexes are far more stable in acidic solutions. This makes metal-exchange studies possible at lower pH values.

Further, the replacement of aliphatic nitrogens by aromatic ones has a pronounced steric effect upon formation reactions with transition metals.⁶ It is of interest to see whether the same effect will manifest itself in metal-exchange reactions as well.

The present study is concerned with the metal-exchange reaction between *N,N'*-bis(2-picoly)ethylenediaminenickel(II) (NiBPEDA²⁺) and copper(II). BPEDA, structure I, has both aromatic and aliphatic nitrogen dentate sites but is analogous to the purely aliphatic triethylenetetramine (trien) in that it contains four nitrogens positioned such that three five-membered chelate rings can form with a metal ion. The results show the exchange reaction to be affected by the presence of aromatic nitrogens when Cu(II) is the attacking metal. Further, hydrolyzed species of Cu(II) are shown to be kinetically important.

Experimental Section

Reagent. BPEDA was prepared according to procedures previously described.⁶ 2-Pyridylmethyl-2'-aminoethylamine (aminoethylaminomethylpyridine, AEAMP) was prepared as described by Barger,

Zachariasen, and Romary⁷ from 2-aminomethylpyridine and 2-chloroethylamine. The trihydrochloride was prepared and gave the following analysis. *Anal.* Calcd for C₈H₁₆N₃Cl₃: C, 36.87; H, 6.19; N, 16.12. Found: C, 36.99; H, 6.17; N, 16.42. Aqueous solutions of AEAMP·3HCl were standardized potentiometrically against standard carbonate-free sodium hydroxide.

All other chemicals were reagent grade and were used without further purification. All solutions were prepared with deionized distilled water. Solutions of NiBPEDA were prepared from standard solutions of NiCl₂ and BPEDA containing 5% molar excess of Ni(II). The solution pH was adjusted to 10, the excess metal was removed as the hydroxide, and the solution pH was lowered to 5.

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

A spectral study of all reactants and products showed the greatest change in molar absorptivity to be at 610 nm. All kinetic measurements were made at this wavelength. The molar absorptivities of reactants and products at 610 nm, $\mu = 0.1$ M, and 25° are as follows: NiCl₂, 0.1; NiBPEDA, 4.17; CuBPEDA, 154. The molar absorptivity of copper solutions varied with pH going from 1.10 at pH 3.9 to 1.49 at pH 5.41.

The rate of reaction of eq 1 was studied by following the increase in absorbance due to the formation of CuBPEDA²⁺. 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 always in a 10-fold excess or greater compared to NiBPEDA²⁺ and covered eight concentrations between 4.40×10^{-3} and 1.74×10^{-2} M over a pH range of 3.44–6.07.

All data were obtained at $25.0 \pm 0.1^\circ$ and $\mu = 0.1$ M.

Results**Determination of Ni²⁺ Stability Constants of AEAMP.**

The complex stability constants of Ni²⁺ with AEAMP, described by eq 2 and 3, were obtained using the method of

$$K_1 = \frac{[\text{NiAEAMP}^{2+}]}{[\text{Ni}^{2+}][\text{AEAMP}]} \quad (2)$$

$$K_2 = \frac{[\text{Ni}_2\text{AEAMP}^{4+}]}{[\text{Ni}^{2+}][\text{NiAEAMP}^{2+}]} \quad (3)$$

Bjerrum⁸ described by Jonassen, LeBlanc, and Rogan.⁹ The values of log *K*₁ and log *K*₂ were calculated using the acid dissociation constants determined by Barger, Zachariasen,

(1) R. K. Steinhaus and R. L. Swann, *Inorg. Chem.*, **12**, 1855 (1973), and references contained therein.

(2) J. J. Latterall, M.S. Thesis, Purdue University, 1962.

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

(4) D. W. Gruenwedel, *Inorg. Chem.*, **7**, 495 (1968).

(5) R. G. Lacoste and A. E. Martell, *Inorg. Chem.*, **3**, 881 (1964).

(6) R. K. Steinhaus and Z. Amjad, *Inorg. Chem.*, **12**, 151 (1973).

(7) J. D. Barger, R. D. Zachariasen, and J. K. Romary, *J. Inorg. Nucl. Chem.*, **31**, 1019 (1969).

(8) J. Bjerrum, "Metal Amine Formation in Aqueous Solution," P. Hase and Son, Copenhagen, 1941.

(9) H. B. Jonassen, R. B. LeBlanc, and R. M. Rogan, *J. Amer. Chem. Soc.*, **72**, 4968 (1950).

Table I. Acid Dissociation Constants and Ni²⁺ Stability Constants for AEAMP at $\mu = 0.1 M$ and 25°

Constant	Value	Constant	Value
AEAMP			
pK_1	1.84 ^a	$\log K_1$	11.90 ^b
pK_2	5.91 ^a	$\log K_2$	9.86 ^b
pK_3	9.54 ^a		
dien			
$\log K_1$	10.7 ^c	$\log K_2$	8.2 ^c

^a Reference 7. ^b This work. ^c L. G. Sillen and A. E. Martell, "Stability Constants of Metal Ion Complexes," The Chemical Society, London, 1964.

and Romary and are listed in Table I. The values for both K_1 and K_2 are higher than the corresponding ones for the nickel complexes of diethylenetriamine,¹⁰ shown in Table I, suggesting that the aromatic nitrogens in conjunction with aliphatic ones may bind more strongly than the purely aliphatic nitrogen ligands.

Kinetic Measurements. The reaction of NiBPEDA²⁺ with Cu_T was found to obey the first-order rate equation

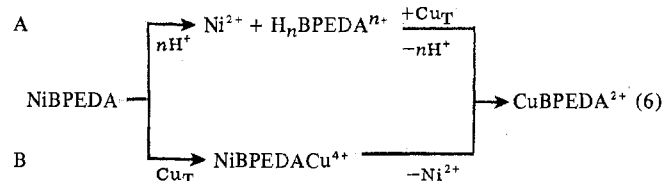
$$-\frac{d[\text{NiBPEDA}^{2+}]}{dt} = k_0[\text{NiBPEDA}^{2+}] \quad (4)$$

where k_0 represents the pseudo-first-order rate constant. Since all reactions were carried out under conditions of at least 10-fold excess Cu(II)

$$k_0 = k_{\text{Cu}_T}^{\text{NiBPEDA}} [\text{Cu}_T] \quad (5)$$

where Cu_T refers to the sum of the kinetically active copper species. After the kinetic behavior of the system was well established, the method of initial rates was used to determine k_0 because $t_{1/2}$ ranged from 4.8 to 8.8 hr.

Resolution of the Rate Data. The formation of CuBPEDA²⁺ from NiBPEDA²⁺ and Cu_T may proceed through either or both of two pathways as shown in eq 6.



The contribution of pathway A to the total exchange rate can be calculated since the kinetics of the formation of NiBPEDA²⁺ from Ni²⁺ and BPEDA, HBPEDA⁺, and H₂BPEDA²⁺ has been studied⁶ and the stability constant associated with each reaction can be calculated. These species have been shown to be kinetically important in the formation of NiBPEDA²⁺; thus the dissociation of NiBPEDA²⁺ must follow the same pathway and the rate of dissociation at constant pH can be written as shown in eq 7. Values of k^{NiL} ,

$$\begin{aligned}
 \frac{d[\text{NiL}]}{dt} &= k_d[\text{NiL}] = k^{\text{NiL}}[\text{NiL}] + k_{\text{H}}^{\text{NiL}}[\text{NiL}][\text{H}^+] + \\
 & k_{2\text{H}}^{\text{NiL}}[\text{NiL}][\text{H}^+]^2 \quad (7)
 \end{aligned}$$

$k_{\text{H}}^{\text{NiL}}$, and $k_{2\text{H}}^{\text{NiL}}$ can be calculated using the known values of formation rate constants and equilibrium constants listed in Table II. The dissociation term, k_d , becomes negligible above pH 4.5. Below pH 4.5 the observed rate constant, k_0 , is corrected for dissociation by subtraction of k_d .

(10) L. G. Sillen and A. E. Martell, "Stability Constants of Metal Ion Complexes," The Chemical Society, London, 1964.

Table II. Stability Constants and Formation Rate Constants for Individual Species of the NiBPEDA²⁺ System at $\mu = 0.1 M$ and 25°

Reaction	$K_{\text{NiL}}^{\text{Ni,H}_n\text{L}}$	$k_{\text{Ni}}^{\text{H}_n\text{L}}$, ^a $M^{-1}\text{sec}^{-1}$	$K_{\text{H}_n\text{L}}$ ^b
Ni ²⁺ + L	2.52×10^{14}	1.82×10^3	
Ni ²⁺ + HL ⁺	1.91×10^8	2.62×10^2	
Ni ²⁺ + H ₂ L ²⁺	2.96×10^5	1.15×10^2	
HL → H + L			5.25×10^{-9}
H ₂ L → H + HL			3.39×10^{-6}

^a Reference 6. ^b Reference 4.

Pathway B involves a direct copper attack on partially dissociated NiBPEDA²⁺. Plots of $k_0 - k_d$ against pH at six different total copper concentrations, shown in Figure 1, indicate that the exchange reaction is sensitive to both pH and copper concentration. The rate, however, varies inversely with [H⁺], not directly as would be expected if [H⁺] were attacking the partially dissociated BPEDA. Thus, the pH behavior rules out proton-assisted dissociation which is not surprising since the terminal dentate sites, which are first to unwrap from NiBPEDA²⁺, are pyridyl groups with pK_a values <2. Further, no stable protonated complexes such as NiBPEDA^H³⁺, analogous to the known Ni(trien)H³⁺, have been found.

Another possible explanation for the inverse [H⁺] behavior would be the existence of hydroxo complexes of NiBPEDA²⁺. Such species do exist in the case of Ni(trien)²⁺ but only above pH 9.¹¹ It is most unlikely that replacement of two terminal aliphatic nitrogens by pyridyl groups cause a shift in hydrolysis of 6 pK units.

The most likely explanation for the inverse hydrogen ion effect involves the attack of hydrolyzed copper species on NiBPEDA²⁺. There are both thermodynamic and kinetic evidences for their existence. Many hydrolyzed species have been proposed, for example, CuOH⁺, Cu₂(OH)₂²⁺, Cu₃(OH)₂⁴⁺, Cu₂OH³⁺, and Cu_n(OH)_{2n-2}²⁺.¹²⁻¹⁴ Previous studies^{2,3} of the analogous exchange reactions between Ni(dien), Ni(trien), and Ni(tetren) and Cu_T have shown CuOH⁺ and Cu₂(OH)₂²⁺ to be kinetically active. Further, the exchange of Cu_T with ZnEDTA²⁻ and with NiEDTA²⁻ proceeds through a pathway involving CuOH⁺.¹⁵ Thus, eq 8 is descriptive of

$$\begin{aligned}
 (k_0 - k_d)[\text{NiBPEDA}^{2+}] &= k_{\text{Cu}}^{\text{NiL}}[\text{Cu}^{2+}][\text{NiBPEDA}^{2+}] + \\
 & k_{\text{CuOH}^+}^{\text{NiL}}[\text{CuOH}^+][\text{NiBPEDA}^{2+}] + \\
 & k_{\text{Cu}_2(\text{OH})_2}^{\text{NiL}}[\text{Cu}_2(\text{OH})_2^{2+}][\text{NiBPEDA}^{2+}] \quad (8)
 \end{aligned}$$

the most likely terms involved in the exchange pathway as well as being consistent with the observed pH and copper concentration behavior. By use of the relation

$$\beta_{mn} = \frac{[\text{Cu}_m(\text{OH})_n^{(2m-n)+}][\text{H}^+]^n}{[\text{Cu}^{2+}]^m} \quad (9)$$

eq 8 may be rewritten as

$$\begin{aligned}
 k_0 - k_d &= (k_{\text{Cu}}^{\text{NiL}} + k_{\text{CuOH}^+}^{\text{NiL}} \frac{\beta_{11}}{[\text{H}^+]}) + \\
 & k_{\text{Cu}_2(\text{OH})_2}^{\text{NiL}} \beta_{22} \frac{[\text{Cu}^{2+}]}{[\text{H}^+]^2} [\text{Cu}^{2+}] \quad (10)
 \end{aligned}$$

(11) D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, **3**, 382 (1964).

(12) H. Ohtaki and T. Kawai, *Bull. Chem. Soc. Jap.*, **45**, 1735 (1972).

(13) D. D. Perrin, *J. Chem. Soc.*, 3189 (1960).

(14) K. J. Pederson, *Kgl. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, **20**, 1 (1939).

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

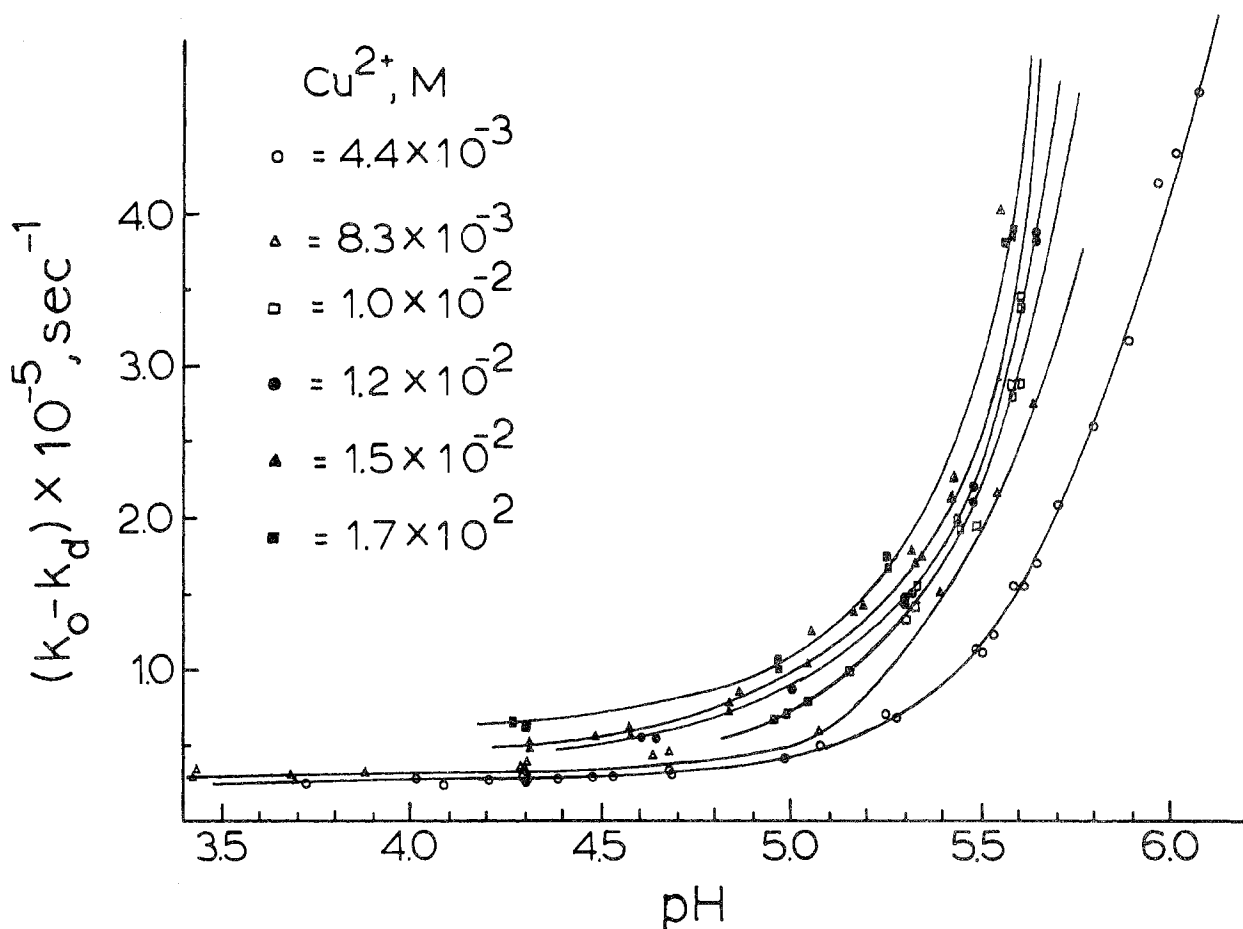


Figure 1. pH dependence of the exchange reaction ($\mu = 0.1 M$, 25°).

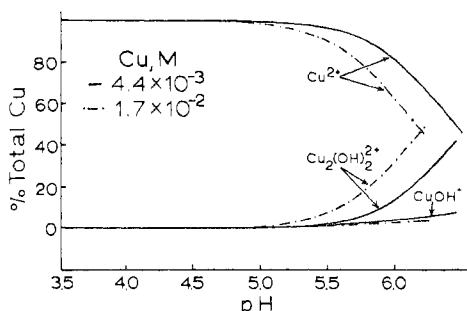


Figure 2. Distribution of copper species as a function of pH at two different total copper concentrations. Calculations are based on eq 11.

The free copper concentration at any pH and total copper concentration can be calculated from eq 11 using known

$$[\text{Cu}]_{\text{total}} = [\text{Cu}^{2+}] + [\text{CuOH}^+] + 2[\text{Cu}_2\text{OH}^{3+}] + 2[\text{Cu}_2(\text{OH})_2^{2+}] \quad (11)$$

values of the formation constants for each species corrected to $0.1 M$ ionic strength. The values used are $\beta_{11} = 5.0 \times 10^{-8}$, $\beta_{21} = 1.4 \times 10^{-6}$, and $\beta_{22} = 2.5 \times 10^{-11}$ which are derived from the values determined by Ohtaki and Kawai.¹² Other known hydrolyzed species such as $\text{Cu}_3(\text{OH})_2^{4+}$, $\text{Cu}_3(\text{OH})_4^{2+}$, and $\text{Cu}(\text{OH})_2$ were initially included but under the conditions of this study were not present in significant amounts. Figure 2 shows the distribution of species for the conditions of this study. Although $\text{Cu}_2\text{OH}^{3+}$ was included in the calculation, it does not appear in Figure 2 because it is too small.

At low pH and low total copper concentrations dimerization is slight and the last term on the right side of eq 10 can be neglected. Equation 10 then rearranges to

$$\frac{k_o - k_d}{[\text{Cu}^{2+}]} = k_{\text{Cu}^{2+}, \text{NiL}} + k_2 \beta_{11} \frac{1}{[\text{H}^+]} \quad (12)$$

Figure 3 shows a least-squares plot of eq 12 for the pH range 3.7–4.5 at a constant total copper concentration of $4.404 \times 10^{-3} M$. The intercept yields a value of $k_{\text{Cu}^{2+}, \text{NiL}} = 4.9 \times 10^{-4} M^{-1} \text{sec}^{-1}$ and the slope a value of $k_{\text{CuOH}^+, \text{NiL}} = 1.1 \times 10^{-1} M^{-1} \text{sec}^{-1}$. The value of $k_{\text{Cu}^{\text{NiL}}}$ can be inserted into eq 10 and rearranged as shown in eq 13. A plot of eq 13,

$$(k_o - k_d - k_{\text{Cu}^{2+}, \text{NiL}} [\text{Cu}^{2+}]) \frac{[\text{H}^+]}{[\text{Cu}^{2+}]} = (k_{\text{CuOH}^+, \text{NiL}}) \beta_{11} + k_{\text{Cu}_2(\text{OH})_2^{2+}, \text{NiL}} \frac{[\text{Cu}^{2+}]}{[\text{H}^+]} \beta_{22} \quad (13)$$

shown in Figure 4 for the pH range 4.9–6.1 and at total copper concentration of $4.404 \times 10^{-3} M$, gave a value of $7.2 \times 10^{-2} M^{-1} \text{sec}^{-1}$ for $k_{\text{Cu}_2(\text{OH})_2^{2+}, \text{NiL}}$.

Since $\text{Cu}_2(\text{OH})_2^{2+}$ is a dimer of CuOH^+ , eq 14 could explain the pH behavior with only Cu^{2+} and CuOH^+ as reactive species. A plot of $(k_o - k_d)/[\text{Cu}^{2+}]$ against $[\text{CuOH}^+](1 + 2[\text{Cu}(\text{OH}^+) \beta_{22}/\beta_{11}^2])/[\text{Cu}^{2+}]$, shown in Figure 5, covering

$$k_o - k_d = k_{\text{Cu}^{2+}, \text{NiL}} [\text{Cu}^{2+}] + k_{\text{CuOH}^+, \text{NiL}} ([\text{CuOH}^+] + 2[\text{Cu}_2(\text{OH})_2^{2+}]) = k_{\text{Cu}^{2+}, \text{NiL}} [\text{Cu}^{2+}] + k_{\text{CuOH}^+, \text{NiL}} [\text{CuOH}^+] (1 + 2[\text{CuOH}^+] \frac{\beta_{22}}{\beta_{11}^2}) \quad (14)$$

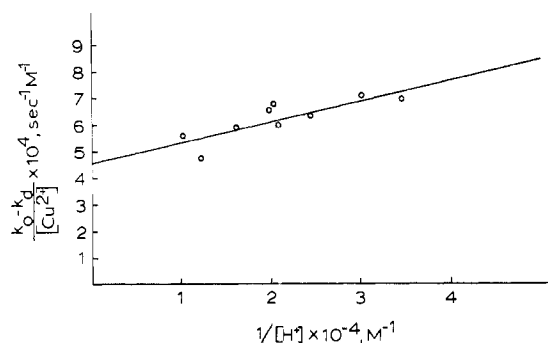


Figure 3. Resolution of $k_{Cu^{2+},NiL}$ and $k_{CuOH^+,NiL}$ using eq 12 ($\mu = 0.1 M$, 25°). Data were taken from the exchange reaction with a total copper concentration of $4.404 \times 10^{-3} M$.

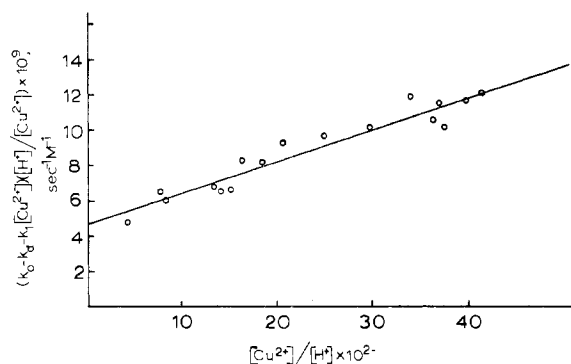


Figure 4. Resolution of $k_{Cu_2(OH)_2^{2+},NiL}$ using eq 13 ($\mu = 0.1 M$, 25°). Data were taken from the exchange reaction with total copper concentration of $4.404 \times 10^{-3} M$.

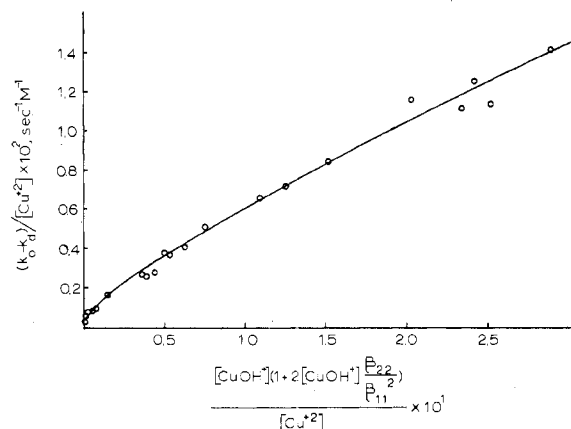


Figure 5. Plot of eq 14 showing that both $CuOH^+$ and $Cu_2(OH)_2^{2+}$ are kinetically active.

the pH range 3.7–6.1 with the total copper concentration at $4.404 \times 10^{-3} M$, is not linear. Thus, $Cu_2(OH)_2^{2+}$ is a reactive species.

The resolved values of $k_{Cu^{2+},NiL}$, $k_{CuOH^+,NiL}$, and $k_{Cu_2(OH)_2^{2+},NiL}$ along with k_d can be used to construct a theoretical curve of k_o against pH from eq 9 at a total copper concentration of $4.404 \times 10^{-3} M$. The computer-generated curve is compared to the experimentally determined values in Figure 6. Excellent agreement is seen over the entire pH range. However, calculated values of k_o from eq 9 at the higher copper concentrations shown in Figure 1 give marked deviation from the experimental values. Comparisons of these experimentally determined points to the theoretical curves generated by a computer show the predicted k_o values to be higher than the experimental ones in all cases. Inclusion of other known hydrolyzed copper species in cal-

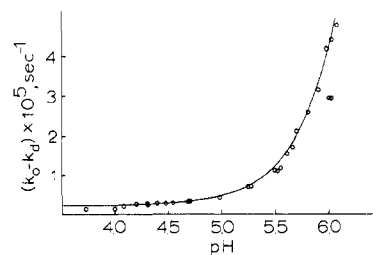


Figure 6. Fit of theoretical curve to experimental rate constants at a total copper concentration of $4.404 \times 10^{-3} M$. Solid line is the curve predicted from eq 9; circled points are experimentally observed values.

culating concentrations of Cu^{2+} , $CuOH^+$, and $Cu_2(OH)_2^{2+}$ did not give a better fit to the data. The most likely explanation for this behavior is the existence of higher order polynuclear hydrolyzed copper species such as those proposed by Perrin, $Cu_n(OH)_{2n-2}^{2+}$.¹³ These species have not been characterized but would become important at both higher total copper and higher pH and thus lower the concentrations of Cu^{2+} , $CuOH^+$, and $Cu_2(OH)_2^{2+}$ which would cause lower experimental values of k_o . For example, although known constants show $Cu_3(OH)_4^{2+}$ to be present only in very small amounts, its concentration increases by a factor of 60 at pH 5 in going from 4.4×10^{-3} to $1.7 \times 10^{-2} M Cu_T$. Also, at $1.7 \times 10^{-2} M Cu_T$ the concentration of $Cu_3(OH)_4^{2+}$ increases by a factor of 750 in going from pH 5 to pH 6. Thus, other unknown species which may be present as well as more accurate constants for known species could markedly affect the distribution of copper species at high copper concentrations.

Discussion

Mechanism of the Exchange Reaction. The resolved rate constants show the exchange reaction, corrected for dissociation, to be first order in a copper species for each rate constant. Thus, copper must be involved either during or before the rate-determining step and clearly prior to complete dissociation of $NiBPEDA^{2+}$. The transfer of $BPEDA$ from Ni^{2+} to Cu^{2+} , analogous to all other dissociation and exchange reactions, most likely proceeds in a stepwise sequence of bond rupture from the departing metal and bond formation, limited by water loss, to the attacking metal. Due to the extreme lability of copper formation reactions, $k^{-H_2O} = 3 \times 10^8 \text{sec}^{-1}$,¹⁶ and the pronounced sluggish rate of exchange seen in this study, pure bond formation to copper cannot be rate limiting.

The proposed mechanism involves stepwise dissociation of $BPEDA$ from Ni^{2+} , followed by coordination of free dentate sites to copper where sterically possible. This gives rise to a series of dinuclear intermediates having one of the dissociation steps along the series as rate determining.

Previous metal-exchange studies have shown that the nature 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 as shown in the equation^{16,17}

$$\frac{k_{Cu}^{NiBPEDA}}{k_{Cu}^{NiL}} = \frac{K_R^{NiBPEDACu}}{K_R^{NiLCu}} \quad (15)$$

(16) M. Eigen and L. DeMaeyer, "Technique of Organic Chemistry," Vol. VIII, A. Weissberger, Ed., 2nd ed, Interscience, New York, N. Y., 1963, Part II, pp 1042, 1047.

(17) T. J. Bydalek and D. W. Margerum, *Inorg. Chem.*, 2, 678 (1963).

where

$$K_R = \frac{(K_{\text{Ni segment}})(K_{\text{Cu segment}})}{K_{\text{Ni complex}}} \quad (16)$$

This involves a knowledge of the stability constants of the nucleophile with various ligands. Since these values are known for nickel and copper, but not for hydrolyzed copper species, only the term and pathway involving free copper will be analyzed in detail.

The systems chosen for comparison are the copper exchange with NiEDDA,¹ with Ni(trien),³ and with NiEDTA.¹⁸ In all of these systems, the rate-determining step has been shown to be the breakage of a nickel-aliphatic nitrogen bond. In the present study both aromatic and aliphatic nitrogens are involved; thus some proposed intermediates involve nickel-aromatic nitrogen bond rupture. Since these are compared to systems having nickel-aliphatic nitrogen bond rupture, a correction for the increased lability of nickel-aromatic nitrogen bonds is needed. The ratio of the rate of dissociation of Ni(py) to Ni(NH₃) represents this difference and amounts to a factor of 7.¹⁹ Electrostatic and statistical corrections are included where appropriate.

A comparison of possible likely dinuclear intermediates for the exchange of NiBPEDA²⁺ with Cu²⁺ to the known systems previously mentioned is made in Table III. Values of K_R , K_{el} , and the statistical factor are included. The last row in Table III shows the ratio of experimental rate constants. The values of K_R were calculated from known stability constants chosen to be as internally consistent as possible with respect to temperature and ionic strength and are listed in Table IV along with experimental values of the rate constants. A comparison of the ratio of experimental rate constants to the predicted ratios of intermediate stability constants shows that structures III and VII give predicted values which agree closely to the experimental rate constant ratios in all cases. Other structures listed in Table III as well as some not listed were tested and gave values which are off by orders of magnitude.

Of the two possible intermediate structures, VII involves dissociation of BPEDA at both ends with an AMP segment chelated to copper and at the opposite end of the complex a free pyridyl group. This is highly unlikely since stability constants of nickel with aromatic-aliphatic mixed ligands exhibit little loss and in some cases a gain by replacing an aliphatic nitrogen by an aromatic one as shown in Table V. Thus, there appears to be no strain in the bonding of an AMP segment to nickel and, therefore, no reason for it to dissociate in a manner such as structure VII would dictate. Structure III however, is not without its peculiarities in that copper is bonded to an internal aliphatic nitrogen and not chelated to the pyridyl group. Unlike nickel, the replacement of an aliphatic nitrogen with an aromatic one does markedly decrease the stability of copper complexes. In fact, Cu(dien), $K = 10^{16}$, is practically as stable as CuBPEDA, $K = 10^{16.3}$. Table V shows the comparisons. Thus, it is not unreasonable to suggest some type of strain or hindrance which prevents copper from chelating to the free AMP segment of BPEDA in intermediate III. Finally, structure III gives the best agreement to the ratio of experimental rate constants.

On this basis a mechanism for the metal exchange of Ni-

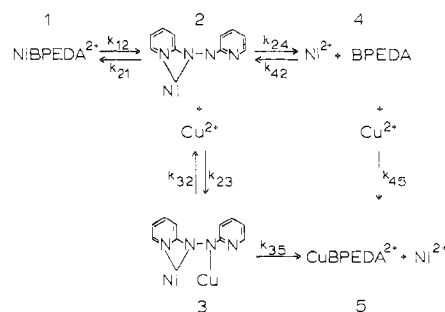


Figure 7. Proposed stepwise mechanism for the exchange of BPEDA between Ni and Cu. Protons are omitted for the sake of clarity.

BPEDA²⁺ and copper can be proposed. This is shown in Figure 7 with protons omitted for the sake of clarity. Step 35 is the rate-determining step, immediately following intermediate 3. Further, the sequence 1, 2, 4, 5 is nearly negligible and can be corrected for from prior knowledge of the dissociation of NiBPEDA²⁺.

The copper-dependent exchange pathway must be 1, 2, 3, 5. A general kinetic expression for the pathway can be written by assuming the steady-state approximation for species 2 and 3

$$\frac{d[\text{NiBPEDA}^{2+}]}{dt} = k_o [\text{NiBPEDA}^{2+}] = k_{35} [3] \quad (17)$$

$$k_o = \frac{k_{21}k_{23}k_{35} [\text{Cu}^{2+}]}{k_{21}k_{32} + k_{21}k_{35} + k_{23}k_{35} [\text{Cu}^{2+}]} \quad (18)$$

Expression 18 reduces to (19) since $k_{21}k_{32} \gg k_{21}k_{35}$ and $> k_{23}k_{35} [\text{Cu}^{2+}]$ at $[\text{Cu}^{2+}] \leq 10^{-2} M$. Thus, the expression

$$k_o = k_{\text{Cu}^{2+}, \text{NiBPEDA}} [\text{Cu}^{2+}] = \frac{k_{12}k_{23}k_{35} [\text{Cu}^{2+}]}{k_{21}k_{32}} \quad (19)$$

derived from the proposed mechanism fits the experimental behavior.

Confirmation of the structure of species 3 may now be obtained knowing the kinetic expression for the mechanism. It is possible to predict the value of $k_{\text{Cu}^{2+}, \text{NiBPEDA}}$ from the relative stability constant of species 3 and an accurate value of k_{35} . This assumes, as seen in eq 19, that the steps prior to the rate-determining step are essentially in equilibrium and we can write

$$k_{\text{Cu}^{2+}, \text{NiBPEDA}} = K_R k_{35} \quad (20)$$

The value of K_R is 1.2×10^{-3} for species 3. An accurate estimate of k_{35} can be obtained from the hydrogen-assisted dissociation of Ni(*N*-pren), where *N*-pren is NH₂CH₂CH₂-NHCH₂CH₂CH₃. Under strong acidic conditions protonation of the secondary nitrogen occurs immediately upon bond rupture making the first bond rupture rate determining rather than the last.²⁰ Thus, $k_{35} = 3 \times 10^{-1} \text{ sec}^{-1}$ and $k_{\text{Cu}^{2+}, \text{NiBPEDA}} = 1.2 \times 10^{-3} \times 10^{-1} \times 3 = 4 \times 10^{-4} M^{-1} \text{ sec}^{-1}$. The agreement between this predicted value and the experimentally observed one $4.9 \times 10^{-4} M^{-1} \text{ sec}^{-1}$ is excellent.

The rate constants involving CuOH⁺ and Cu₂(OH)₂²⁺ show enhanced behavior due to the presence of hydroxide as seen in Table VI. The accelerating effect of hydrolyzed copper species has been seen in other systems.^{2,3,15} If the same mechanism proposed for free copper is assumed to hold for the hydrolyzed species, then the enhancement in rate could

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Table III. Comparison of Possible Likely Dinuclear Intermediates for the Exchange of NiBPEDA²⁺ with Cu²⁺ to Known Systems

No.	Ni(trien)-Cu		NiEDDA-Cu		NiEDTA-Cu	
	NiBPEDA-Cu	K_R	$\frac{K_R^{\text{NiBPEDA-Cu}}}{K_R^{\text{Ni(trien)-Cu}}}$	$\frac{K_R^{\text{NiBPEDA-Cu}}}{K_R^{\text{NiEDDA-Cu}}}$	$\frac{K_R^{\text{NiBPEDA-Cu}}}{K_R^{\text{NiEDTA-Cu}}}$	
		$K_R = 8$				
		$K_R = 4 \times 10^{-1}$				
		$K_R = 6 \times 10^{-3}^a$				
I		8×10^{-1}	1×10^{-1}	2	2×10	
II		2×10^{-5}	2×10^{-6}	4×10^{-5}	4×10^{-4}	
III		1×10^{-3}	1.5×10^{-4}	3×10^{-3}	3×10^{-2}	
IV		3×10^2	3×10^1	8×10^2	8×10^3	
V		6×10^{-13}	$5 \times 10^{-13}^b$	$1 \times 10^{-11}^b$	$1 \times 10^{-10}^b$	
VI		5×10^{-3}	$4 \times 10^{-3}^b$	$7 \times 10^{-2}^b$	$7 \times 10^{-1}^b$	
VII		8×10^{-3}	1×10^{-3}	2×10^{-2}	2×10^{-1}	
VIII		1×10^2	7×10^b	$3 \times 10^3^b$	$3 \times 10^{-3}^b$	
	$k_{\text{Cu}}^{\text{NiBPEDA}}/k_{\text{Cu}}^{\text{NiL}}$		2×10^{-4}	7×10^{-3}	6×10^{-3}	

^a The statistical factor of 2 and $K_{\text{el}} = 3.16$ are figured into this value of $K_R^{\text{NiEDTA-Cu}}$. ^b These values include a factor of 7 for the ratio of Ni-NH₃ to Ni-py bond breakage.

be explained by an increase in the relative stability of intermediate 3. Numerous examples can be found illustrating an increase in stability for reactions such as eq 21. Those



pertinent to the present system are listed in Table VII. In all cases, however, the addition of a hydroxide to the complex increases the stability between 10^4 and 10^5 , but the use of CuOH^+ as a reactant decreases the stability by 10^8 .

Therefore there is not a net gain but a loss of about 10^2 in stability due to CuOH^+ which would result in a decrease in the rate.

Another possible explanation is the assumption that intermediate 3 is a transition state rather than an intermediate. If true, then an increase in the rate of water loss from copper due to hydroxide could increase the reaction rate. An increased lability of coordination compounds due to hydroxide has been seen with Co(III),^{21a} Cr(III),^{21b} and Fe(III)^{21c} compounds but never for Cu(II). In fact, the reaction of tetren with CuOHtrien^+ is slower by a factor of 2 compared

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Table IV. Stability Constants and Rate Constants Used in Making Comparisons Shown in Table III^a

Ligand	$\log K_{\text{NiL}}$	$\log K_{\text{CuL}}$	$k_{\text{NiCuL}}, M^{-1} \text{ sec}^{-1}$
BPEDA	14.4 ^b		$4.9 \times 10^{-4} c$
EDDA	13.5		$7.0 \times 10^{-2} d$
EDTA	18.6		$7.5 \times 10^{-2} e$
trien	14.1		2.7^f
AMP	7.2	9.6	
AEAMP	11.9 ^c	14.6 ^g	
en	7.5	10.6	
dien	10.7	16.0	
Glycine	5.3	7.6	
IDA		11.1	
NH ₃	2.7	4.3	
py	1.8	2.4	

^a All values either are at 25° and $\mu = 0.1 M$ or are chosen to be as close to these conditions as possible. Except as noted all values are taken from ref 10. ^b Reference 4. ^c This work. ^d Reference 1. ^e T. J. Bydalek and D. W. Margerum, *J. Amer. Chem. Soc.*, 83, 4326 (1961). ^f Reference 3. ^g Reference 7.

Table V. Comparison of Stability Constants between Aliphatic and Aromatic Nitrogen Complexes with Nickel(II) and Copper(II)^a

Ligand	$\log K_{\text{CuL}}^{\text{Cu, L}}$	$\log K_{\text{aliphatic}} - \log K_{\text{aromatic}}$
	Copper	
NH ₃	4.3	+1.9
py	2.4	
en	10.6	+1.0
AMP	9.6	
dien	16.0	+1.4
AEAMP	14.6 ^b	
trien	20.5	+4.2
BPEDA	16.3 ^c	
	Nickel	
NH ₃	2.7	+0.9
py	1.8	
en	7.5	+0.3
AMP	7.2	
dien	10.7	-1.2
AEAMP	11.9	
trien	14.1 ^d	-0.3
BPEDA	14.4 ^c	

^a All values at 25° and $\mu = 0.1 M$. All values from ref 10 except as noted. ^b Reference 7. ^c Reference 4. ^d This work.

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

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

^a H. B. Jonassen, R. E. Reeves, and L. Sogal, *J. Amer. Chem. Soc.*, 77, 2748 (1955). ^b R. L. Gustafson and R. E. Martell, *ibid.*, 81, 525 (1959). ^c J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, 33, 985 (1950). ^d R. C. Courtney, R. L. Gustafson, S. Chaberck, and A. E. Martell, *J. Amer. Chem. Soc.*, 81, 519 (1959).

Table VII. Comparison of Rate Constants for the Attack of Cu²⁺ and CuOH⁺ on Various Complexes^a

Complex	$k_{\text{Cu}^{2+}\text{NiL}}$	$k_{\text{CuOH}^+\text{NiL}}$ ^b	$k_{\text{CuOH}^+\text{NiL}} / k_{\text{Cu}^{2+}\text{NiL}}$
NiBPEDA ²⁺	$4.9 \times 10^{-4} c$	0.1080 ^c	220
Ni(trien) ²⁺	2.7 ^d	80 ^d	30
NiEDTA ²⁻	0.075 ^e	1.4 ^{e,f}	18
ZnEDTA ²⁻	67 ^e	220 ^e	33

^a All rate constants in $M^{-1} \text{ sec}^{-1}$ at 25° and $\mu = 0.1 M$. ^b Values of $k_{\text{CuOH}^+\text{NiL}}$ have been calculated assuming $\beta_{11} = 5 \times 10^{-8}$. ^c This work. ^d Reference 3. ^e Reference 15. ^f The data used to resolve $k_{\text{Cu}^{2+}\text{NiEDTA}^{2-}}$ and $k_{\text{CuOH}^+\text{NiEDTA}^{2-}}$ were not corrected for any hydrolyzed copper species.

to its reactions with Cu(trien), after correcting for statistical factors.²²

Due to rapid Jahn-Teller inversion,²³ hydroxide, which initially reacted with an axial water to form CuOH⁺, would immediately occupy an equatorial site. Subsequent bonding to CuOH⁺ would occur at the "new" axial sites since loss of equatorial water is very sluggish compared to loss of axial water.¹¹

It is most likely that the Jahn-Teller effect prevents equatorial hydroxide from affecting the loosely held axial waters. Evidence for this is found in a study of the formation of mixed-ligand species from Ni(5-X-phen) and dien or NTA.²⁴ The study showed the effect of substituents at an equatorial site to be transmitted to other equatorial sites by a factor of 3 times greater than to axial sites. In nickel, all six sites are approximately equal, yet axial sites are less affected than equatorial ones. Thus, with copper, where axial waters are weakly bound compared to equatorial waters, very little if any effect would be transmitted to them.

Finally, there appears to be less than a factor of 10 between the rate of water loss for copper and a diffusion-limited process,²⁵ so that even if hydroxide somehow could enhance the water loss rate, the enhancement would be nowhere near the factor of 100 seen in this study.

The most likely possibility for the enhanced rate of attack of CuOH⁺ and Cu₂(OH)₂²⁺ is the formation of some type of hydrogen-bonded or hydroxide-bridged intermediate. The hydroxide oxygen could form a hydrogen bond to a proton of one of the waters on nickel or could form a hydroxide bridge with nickel. This phenomenon is not uncommon.²⁶ Repulsion of charges appears not to be important because of the stability of Cu₂(OH)₂²⁺ and other similar species such as Cr₂(OH)₂⁴⁺, Fe₂(OH)₂⁴⁺, and Co₂(OH)₂⁴⁺.¹⁶ Thus either an added degree of stability can be imparted to intermediates preceding the rate-determining step or nickel-nitrogen bond breakage could be labilized due to the interaction with hydroxide. This phenomenon is not unlike the ICB mechanism which appears to impart added stability during formation reactions.²⁷ Systems showing an ICB effect have involved weak bases yet show gains of 10 and 20 in reaction rate. Also, the presence of aromatic nitrogens in the nickel coordination sphere has been shown to enhance the ICB effect.²⁸ The present system involves a strong base, hydroxide, and does have an aromatic nitrogen in the coordination sphere. Thus, an ICB-like effect involving hydrogen bonds or hydroxide bridges could cause a corresponding large increase on rate.

Analogous metal-exchange systems involving copper as the attacking nucleophile also show enhanced rates due to CuOH⁺. Table VII lists the values. In all cases, not involving aromatic nitrogens bonded to nickel, it can be seen that CuOH⁺ is about 30 times more reactive than Cu²⁺. The added factor of 7 between these complexes and NiBPEDA²⁺ could be attributed to the presence of an aromatic nitrogen in BPEDA, since, as previously mentioned, aromatic nitrogens

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increase the ICB effect. The reactions involving NiEDTA, Ni(trien), and NiBPEDA all have nickel-nitrogen bond rupture as rate determining while the ZnEDTA system involves copper-ligand bond formation as rate determining. Of the three possible explanations for the increased activity due to CuOH^+ , the first, an increase in the stability of the dinuclear intermediate, cannot explain why CuOH^+ reacts at an accelerated rate with ZnEDTA because the dinuclear intermediate forms after the rate-determining step. The second explanation, a transition state, could explain all four systems but is

based on the tenuous grounds of an acceleration in copper water loss due to hydroxide. The third possibility, however, fits all four cases since a hydrogen-bonded or hydroxide-bridged intermediate would affect the values of K_{os} , the outer-sphere association constant, to the same extent that it would affect the stability of a dinuclear intermediate. Therefore it is suggested that this is the most likely explanation for the increased reactivity of CuOH^+ .

Registry No. NiAEAMP²⁺, 52613-52-2; NiBPEDA²⁺, 52613-53-3; Cu^{2+} , 15158-11-9; CuOH^+ , 19650-79-4; $\text{Cu}_2(\text{OH})_2^{2+}$, 12331-89-4.

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Magnetic Exchange Interactions in Transition Metal Dimers. III. Nickel(II) Di- μ -cyanato, Di- μ -thiocyanato, and Di- μ -selenocyanato Complexes and Related Outer-Sphere Copper(II) Complexes

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Complexes with the general formulation $[\text{M}_2(\text{tren})_2\text{X}_2](\text{BPh}_4)_2$, where $\text{M} = \text{Cu(II)}$ and Ni(II) , $\text{tren} = 2,2',2''$ -triaminotriethylamine, and $\text{X}^- = \text{OCN}^-$, SCN^- , and SeCN^- , have been prepared and studied by various physical techniques including magnetic susceptibility and esr. The nickel systems are dimeric with two X anions end-to-end bridging such that the nickel atoms are octahedrally coordinated. There is an antiferromagnetic exchange interaction ($J = -4.4 \text{ cm}^{-1}$) in the cyanate-bridged nickel dimer, whereas both the di- μ -thiocyanate and the di- μ -selenocyanate systems are ferromagnetically coupled ($J = +2.4$ and $+1.6 \text{ cm}^{-1}$, respectively). The exchange interaction in these nickel(II) dimers is discussed in terms of the known structural characteristics of the cyanate and thiocyanate dimers. The coordination geometry for the three XCN^- - Cu^{II} systems is shown to be trigonal bipyramidal by esr studies. Single-crystal X-ray work on one of the two forms of $[\text{Cu}_2(\text{tren})_2(\text{OCN})_2](\text{BPh}_4)_2$ substantiates this and shows that the copper cation in this compound is a dimer (Cu-Cu distance 6.58 Å) by virtue of the cyanate, which is N bonded to one trigonal-bipyramidal copper in the axial position, hydrogen bonding through its oxygen atom with one of the nitrogen atoms of the tren ligand coordinated to the second copper atom. The second form of copper cyanate probably has a somewhat different hydrogen-bonding configuration as a result of a different packing arrangement of copper dimers and tetraphenylborates. While there is no exchange interaction detectable for the $[\text{Cu}_2(\text{tren})_2(\text{XCN})_2](\text{BPh}_4)_2$ compounds in the magnetic susceptibility to 4.2°K, $\Delta M_S = 2$ transitions are seen in the esr spectra of the cyanate and thiocyanate complexes. Additional evidence for the dimeric nature of these copper complexes is found in the identification of esr transitions between their singlet and triplet states (in the ${}^1S_M S$ coupled notation, $|1-1\rangle \rightarrow |00\rangle$ at high field and $|00\rangle \rightarrow |11\rangle$ at low field). The field position of these transitions for the copper thiocyanate dimer gives $|J| = 0.06 \text{ cm}^{-1}$. The two different crystalline forms of $[\text{Cu}_2(\text{tren})_2(\text{OCN})_2](\text{BPh}_4)_2$ have $\Delta M_S = 2$ transitions and temperature-dependent singlet-to-triplet (S \rightarrow T) transitions. Between 330 and 95°K the J value [from S \rightarrow T transition] for one form varies between 0.09 and 0.16 cm^{-1} , while for the second form J varies between 0.05 and 0.06 cm^{-1} . Off-axis extrema are seen in the $\Delta M_S = 1$ region Q-band powder spectra for the three XCN^- -Cu outer-sphere dimers.

Introduction

In the previous two papers in this series^{3,4} the symmetry, distance, and electron configurational effects influencing the magnitude and sign of magnetic exchange interactions in dimeric transition metal complexes have been illustrated. Exchange interactions that are propagated by discrete polyatomic bridging moieties between two paramagnetic centers have been the major concern. The present paper deals with magnetic interactions in both nickel(II) and copper(II) dimers where the metals are dimerized by either cyanate, thiocyanate, or selenocyanate groups. Interesting relationships between rather subtle changes in molecular structure and the net electron-exchange interaction have been detected. Par-

ticularly important is the series of di- μ -azido-, di- μ -cyanato-, di- μ -thiocyanato-, and di- μ -selenocyanato-bridged nickel(II) dimers (we have reported on the di- μ -azido material previously⁴). The bonding and resultant molecular structural differences in this Ni(II) series lead to both net antiferromagnetic (N_3^- and OCN^-) and ferromagnetic (SCN^- and SeCN^-) exchange interactions, the mechanisms for which will be discussed in this paper.

The chemistry and bonding properties of the pseudohalides OCN^- , SCN^- , and SeCN^- have been the subject of several reviews^{5,6} which focus upon the ability of these pseudohalides to coordinate to metals in a variety of ways. When the metal to anion ratio is 1:1, there are seven di- μ - XCN^- bridging possibilities; the three symmetric and most probable bridging modes are I-III.

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