metal ions of the octahedral complexes. On the other hand, there is no unpaired electron in the t_{2g} orbitals of high-spin octahedral Cu^{II} and Ni^{II} complexes and direct π-electron spin delocalization could not be as important in these complexes as in the Fe^{II} and Co^{II} complexes.

Bond lengths in the metal complexes as well as the diamagnetic interactions have already suggested[2] that the stability of the complexes results mainly from strong interactions at $O(4\alpha)$, resulting in direct σ interactions propagated to the NH(3) proton. However, a σ–π spin polarization should occur mainly at N(5) since the pyrimidine moiety is very poorly conjugated to the rest of the isoalloxazine ring. The mechanisms of spin delocalization in paramagnetic complexes do not reflect directly the nature of the organometallic binding but it can be noted that the amount of delocalized π spin is directly related to the stability of the complexes.

A precise knowledge of the mechanism of spin polarization would require extended molecular orbital calculations for the whole complexes. However, PPP SCF molecular orbital calculations[35] for the isolated isoalloxazine ligand suggest that the highest filled π orbital, which should be energetically favored for a polarization process, is a poor candidate because of its very small atomic coefficient at N(5) ($c_N{}^2 = 0.002$).

The indirect mechanism and the weakness of the spin delocalization within the flavoquinone–metal complexes represent a potential barrier for partial or total electron transfer, presumably due to the long distance between N(5) and the metal ion, which may have some implications in biological oxidoreduction processes.

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Registry No. $Fe(TARF)_3(ClO_4)_2$, 55648-61-8; $Fe(H_2O)_6(ClO_4)_2$, 15305-57-4; $Co(TARF)_3(ClO_4)_2$, 55648-63-0; $Co(H_2O)_6(ClO_4)_2$, 15305-50-7; $Ni(TARF)_3(ClO_4)_2$, 55648-65-2; $Ni(H_2O)_6(ClO_4)_2$, 10171-10-5; $(C_{27}H_{32}N_4O_{10}ClO_4H_2O)_2Cu$, 55638-31-8; $Cu(TARF)_2{}^{2+}$, 55648-66-3; $Mn(TARF)^{2+}(H_3CC(O)CH_3)_5$, 55638-28-3; $Co(N^3\text{-Et-TARF})_3{}^{2+}$, 55648-67-4; 3-benzyllumiflavine, 14684-43-6; 3-benzyl-8-norlumiflavine, 55637-99-5; 3-benzyl-7,8-norlumiflavine, 55638-00-1; iron, 7439-89-6; cobalt, 7440-48-4.

References and Notes

(1) M stands for metal and RFl_{ox} is the flavine (isoalloxazine) ligand with R = H or alkyl substituent at N(3).

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Kinetics of Tetraethylenepentamine Ligand Exchange Reactions of Copper(II)–Polyamine Complex Ions[1]

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The rates of the ligand-exchange reactions of tetren with Cu(trien), Cu(dien), and $Cu(dien)_2$ are measured using stopped-flow spectrophotometry and the pH dependence of the reaction rates analyzed. The rate constants for the attack of unprotonated tetren on CuL are 7.47×10^4 and 1.02×10^8 M^{-1} sec^{-1} for L = trien and dien, respectively, at 25° and 0.1 M ionic strength. For the reaction of tetren with Cu(trien), a mechanism is proposed wherein one nitrogen on the incoming ligand is bonded prior to the rate-determining step. For the reaction of tetren with Cu(dien), the rate-determining step is the rate of water loss from the Cu(dien) complex. Comparisons of structural effects are made between this work and studies for the exchange of Cu(tren) with tetren previously conducted in this laboratory.

Introduction

In this work the all-polyamine ligand-exchange reactions of Cu(trien), Cu(dien), and $Cu(dien)_2$ with tetren have been investigated by stopped-flow spectrophotometry (reactions 1–3) and the results contrasted with those of a previous study of the all-polyamine ligand-exchange reactions of Cu(tren) with dien, trien, and tetren conducted in this laboratory[9] (reactions 4–6).

$$\mathrm{Cu(trien)^{2+} + tetren \rightarrow Cu(tetren)^{2+} + trien} \tag{1}$$

$$\mathrm{Cu(dien)^{2+} + tetren \rightarrow Cu(tetren)^{2+} + dien} \tag{2}$$

$$\mathrm{Cu(dien)_2{}^{2+} + tetren \rightarrow Cu(tetren)^{2+} + 2dien} \tag{3}$$

$$\mathrm{Cu(tren)^{2+} + 2dien \rightarrow Cu(dien)_2{}^{2+} + tren} \quad (4)$$

$$\mathrm{Cu(tren)^{2+} + trien \rightarrow Cu(trien)^{2+} + tren} \quad (5)$$

$$\mathrm{Cu(tren)^{2+} + tetren \rightarrow Cu(tetren)^{2+} + tren} \quad (6)$$

For reactions 4–6, the observed rate of exchange was found to increase with increasing pH in the pH region 6.0–9.5 (attributed to deprotonation of attacking ligand) followed by a decrease in the rate of exchange of higher pH values attributed to the slower ligand substitution of Cu(OH)tren. The (30–100)-fold decrease in the observed rate of exchange with $\mathrm{Cu(OH)tren^+}$ compared to $\mathrm{Cu(tren)^{2+}}$ is thought to be due to the trigonal-bipyramidal structure[10] of $\mathrm{Cu(OH)tren^+}$. This structure eliminates all solvent molecules from the inner coordination sphere and permits attack of the incoming ligand only at sites coordinated by hydroxide or the polyamine nitrogens. The $\mathrm{Cu(tren)^{2+}}$ on the other hand is reported to have a *cis*-diaquo octahedral structure[8,11,12] possessing two labile inner-sphere solvent molecules available as sites for attack by the incoming ligand.

The study of reactions 1 and 2 was undertaken to determine the pH dependence of the ligand exchange and to evaluate the relative effects due to the formations of $\mathrm{Cu(OH)trien^+}$ and $\mathrm{Cu(OH)dien^+}$ since the octahedral structures of these species[8] are expected to retain one and two inner-sphere solvent molecules as labile sites for attack by the incoming ligand. Any decrease in the observed rate or exchange due to the formation of these hydroxy species would therefore be expected to be less dramatic.

Experimental Section

In all cases solutions were prepared from redistilled deionized water. tren was commercially obtained as a gift from Jefferson Chemical Co., and the gas chromatographically pure liquid (except for a small amount of water) was used without further purification. Commercial reagent grade $\mathrm{trien{\cdot}2H_2SO_4}$ was recrystallized by cooling a hot solution which had been brought to saturation by the addition of ethanol. dien was precipitated and recrystallized as the hydrochloride salt from a commercially obtained liquid.[13] $\mathrm{tetren{\cdot}2.5H_2SO_4}$ was prepared from the free polyamine and purified by the method of Reilley.[14] A weighed amount of solid copper metal was dissolved in a minimum amount of reagent grade nitric acid and diluted to volume. The resulting solution was standardized electrogravimetrically or by potentiometric titration against standard EDTA using a cupric ion selective electrode. Weighed amounts of each ligand were dissolved in water and standardized by potentiometric titration with standard copper nitrate (tren, trien, and tetren) or titration with standard $\mathrm{HNO_3}$ (dien). The copper–polyamine complexes were prepared by combining stoichiometric volumes of the appropriate standard solutions or by adding a small excess of metal to a standard ligand solution and removing the excess metal by hydroxide precipitation at pH 10. Sodium perchlorate, sodium hydroxide, potassium hydroxide, and all other chemicals used were reagent grade and were used without further purification. Boric acid was recrystallized once from hot water solution.

Absorption spectra of all complexes at 0.25–1.0 pH intervals were recorded on a Cary Model 14 spectrophotometer and molar absorptivities calculated from these spectra. These values were used in the calculation of observed rate constants. The molar absorptivities of Cu(tetren) calculated from equilibrium absorbancies on the stopped-flow spectrophotometer were in excellent agreement with that measured on the Cary. Reactions were monitored with a Durrum-Gibson stopped-flow spectrometer. The amplified signal was opposed by a voltage from a mercury source so that a selected portion of the percent transmittance scale could be fed into a Tektronix Type 564 storage oscilloscope which is equipped with a Type 2A63 differential amplifier and Type 2B67 time base. The stored image was photographed on Polaroid film. Reaction 1 was followed at 310 nm under a variety of concentration ratios and levels with 10- and 20-fold excesses of tetren to give pseudo-first-order reactions. Reaction 2 was followed at 270 nm and reaction 3 at 280 nm using equal initial concentrations. For reaction 1 a borate–boric acid buffer system was used to control the pH. Excess attacking ligand also served to buffer the solution. $\mathrm{NaClO_4}$ was used to control the ionic strength at a value of 0.1 *M*. For reactions 2 and 3, borate and phosphate buffers were used to control the pH. To determine whether the phosphate buffer interfered as a result of the formation of copper–phosphate complexes, particularly at high pH, reaction 2 was tested at pH 8.24 and 12.25 in the presence and absence of phosphate buffer. The oscilloscope traces and observed rate constants were identical within the experimental uncertainties indicating no interference. $\mathrm{KClO_4}$ was used to control the ionic strength at a value of 0.10 *M*.

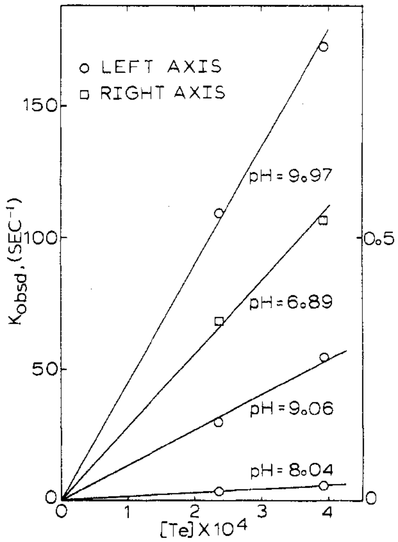

Figure 1. Linear dependence of the observed rate constant $k_{\mathrm{obsd}} = k^{\mathrm{Cu(trien)}}{}_{\mathrm{tetren}}[\mathrm{tetren}]_{\mathrm{t}}$ on excess tetren concentration. The plotted points correspond to the averages for reaction numbers Cu(trien) + tetren = 301–318 as tabulated in Table VI in the microfilm edition.

Results

Pseudo-first-order and second-order rate constants were calculated with the aid of an IBM 360/65 computer. The reactions of tetren with Cu(trien) and Cu(dien) were found to be first order in polyamine and first order in the copper complex (cited below). The general rate equation in terms of total concentration of polyamine and copper complex is given by eq 7 and 8.

For reaction 1 and constant pH

$$\text{rate} = -\frac{\mathrm{d[Cu(trien)]}}{\mathrm{d}t} = k_{\mathrm{obsd}}[\mathrm{Cu(trien)}]_{\mathrm{t}} = k^{\mathrm{Cu(trien)_t}}{}_{\mathrm{tetren_t}}[\mathrm{tetren}]_{\mathrm{t}}[\mathrm{Cu(trien)}]_{\mathrm{t}} \qquad (7)$$

The subscript "t" implies the total or analytical concentration of all forms of species involved. The value of the observed first-order rate constant, k_{obsd}, is linearly dependent on the concentration of free ligand (Figure 1). For reaction 2 at constant pH

$$\text{rate} = -\frac{\mathrm{d[Cu(dien)]}}{\mathrm{d}t} = k^{\mathrm{Cu(dien)_t}}{}_{\mathrm{tetren_t}}[\mathrm{tetren}]_{\mathrm{t}}[\mathrm{Cu(dien)}]_{\mathrm{t}} \qquad (8)$$

and for reaction 3 at constant pH

$$\text{rate} = -\frac{\mathrm{d[Cu(dien)_2]}}{\mathrm{d}t} = k^{\mathrm{Cu(dien)_2}}{}_{\mathrm{tetren_t}}[\mathrm{tetren}]_{\mathrm{t}}[\mathrm{Cu(dien)_2}] \qquad (9)$$

The reaction conditions for reactions 1–3 are given in Table I. All experimental rate constants are given in Tables V–VIII published in the microfilm edition of this journal.[15] These data were used to draw the pH profiles for reaction 1 (Figure 2) and reactions 2 and 3 (Figure 3).

The forward rate constants of reactions 1 and 2 were resolved

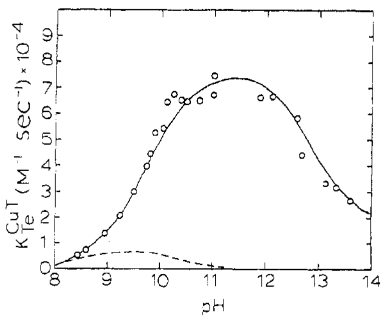

Figure 2. Plot of the second-order rate constant $k^{Cu(trien)_t}{}_{tetren_t}$ as a function of pH. The dashed line corresponds to $k^{Cu(tren)_t}{}_{tetren_t}$ and is included for comparison.

Table I. Reaction Conditions for the Rate Studies of tetren with Cu–trien and Cu–dien Complexes at 25° and $\mu = 0.1$

CuL complex	$[\text{tetren}]_0$, M	$10^4 [\text{CuL}]_0$, M	pH
Cu(trien)^b	3.92×10^{-3}	3.98	6.6–11.0
	2.36×10^{-3}	1.99	6.9–>14^a
	3.92×10^{-3}	1.99	6.9–11.3
	3.92×10^{-3}	3.98	6.8–11.2
Cu(dien)^c	1.00×10^{-5}	0.100	6.9–12.9
Cu(dien)$_2$^{d,e}	1.00×10^{-5}	0.100	6.0–13.2

^{a} $\mu > 0.1$. ^{b} λ 310 nm. ^{c} λ 270 nm. ^{d} λ 280 nm. ^{e} $[\text{dien}]_t$ varied from 1×10^{-5} to 1×10^{-2} M as described in Table III.

into individual proton-dependent terms to fit the equation

$$\begin{aligned} k^{CuL_t}{}_{tetren_t}[\text{tetren}]_t[\text{CuL}]_t = {} & k^{Cu(OH)_2L}{}_{tetren}[\text{tetren}][\text{Cu(OH)}_2\text{L}] + \\ & k^{Cu(OH)L}{}_{tetren}[\text{tetren}][\text{Cu(OH)L}] + \\ & k^{CuL}{}_{tetren}[\text{tetren}][\text{CuL}] + \\ & k^{CuL}{}_{Htetren}[\text{H(tetren)}][\text{CuL}] + \\ & k^{CuL}{}_{H_2tetren}[\text{H}_2\text{tetren}][\text{CuL}] + \\ & k^{CuL}{}_{H_3tetren}[\text{H}_3\text{tetren}][\text{CuL}] \end{aligned} \qquad (10)$$

Calculations of the resolved rate constants were performed with an IBM 360/65 computer using a weighted regression analysis program.[16] Only the terms of eq 10 pertinent to a given system were included in a reported regression analysis. Other terms are known from equilibrium constants or preliminary regression analyses to be unimportant.

Figures 1 and 2 show that the observed second-order rate constants for the tetren reactions with Cu(trien) and Cu(dien) first increase with increasing pH (pH <10–11) and eventually decrease at still higher pH (pH >11). The pH dependence can be expressed in terms of the various protonated tetren species and mixed hydroxy–copper–ligand complexes in solution. The resolved rate constants are shown in Table II. The solid lines in the pH profiles (Figures 2 and 3) were computed using the resolved rate constants and eq 10.

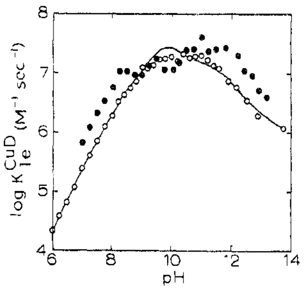

Figure 3. pH profile of the rate constant for tetren substitution of Cu(dien) at 25° and 0.10 M ionic strength. The open circles correspond to reaction 2 and the reaction conditions $[\text{Cu(dien)}]_0 = 1.00 \times 10^{-5}$ M and $[\text{tetren}] = 1.00 \times 10^{-5}$ M. The solid line corresponds to the best fitting line calculated from the resolved rate constants of reaction 2. The closed circles correspond to reaction 3 and the reaction conditions $[\text{Cu}]_t = 1.00 \times 10^{-5}$ M, $[\text{dien}]_t = 1.00 \times 10^{-3}$ M, and $[\text{tetren}]_0 = 1.00 \times 10^{-5}$ M.

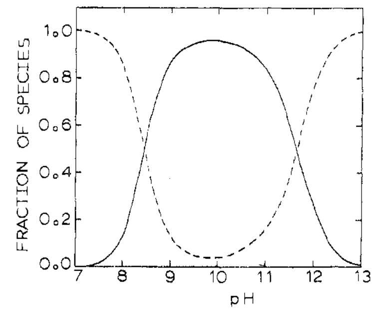

Figure 4. Values calculated for $\alpha_{Cu(dien)_t}$ [for all mono(diethylenetriamine) species including Cu(dien), Cu(OH)dien, and Cu(OH)$_2$dien and $\alpha_{Cu(dien)_2}$ (assumed to exist in only one form)] vs. pH under the reaction conditions $[\text{Cu}]_t = 1.00 \times 10^{-5}$ M and $[\text{dien}]_t = 1.00 \times 10^{-5}$ M.

The Effect of Excess dien on Reaction 2. The pH profile for reaction 2 was repeated in the presence of 100-fold excess dien (reaction 3) to study any effects resulting from the presence of free dien or the formation of the Cu(dien)$_2$ complex. The observed profile (Figure 3) is not dramatically changed from that observed in the absence of excess dien. Comparison of the pH profiles indicates the presence of excess dien speeds the rate of exchange roughly twofold at low pH (pH <8.5) and high pH (pH >11) while the profiles overlap between pH 8.5 and 11.

The Cu(dien)$_2$ complex is only expected to exist in amounts ≥50% in the pH region between pH 8.4 and 11.6 with the free dien concentration used in this study. Figure 4 is a plot of $\alpha_{Cu(dien)_2}$ vs. pH under the reaction conditions employed, calculated using the previously reported stability constant for Cu(dien)$_2$ of log $K^{Cu(dien)}{}_{Cu(dien)_2} = 5.20$,[5] log $K^{Cu(dien)}{}_{Cu(OH)dien} = 4.5$,[8] and the value for log $K^{Cu(OH)dien}{}_{Cu(OH)_2dien} = 1.2$ determined in this work.

To verify further any rate-speeding effect of excess dien, a series of reactions were studied at pH 7.01 in the presence of 0-, 10-, 100-, and 1000-fold excess dien. The reaction

Table II. Resolved Rate Constants for Reactions 1 and 2 at 25° and $\mu = 0.1$

Rate constant	tren^{a,c}	trien^c	dien^d
$k^{Cu(OH)_2L}{}_{tetren}$			0.778 ± 0.21
$k^{Cu(OH)L}{}_{tetren}$	0.51 ± 0.18	17.4 ± 2.0	13.4 ± 0.95
$k^{CuL}{}_{tetren}$	54.1 ± 6.9	74.7 ± 2.1	102 ± 14
$k^{Cu(OH)L}{}_{Htetren}$	[35.0 ± 4.5]^b	[4,680 ± 103]	[31.9 ± 4.5]
$k^{CuL}{}_{Htetren}$	11.1 ± 0.67	29.7 ± 1.7	23.3 ± 3.4
$k^{Cu(OH)L}{}_{H_2tetren}$	[22.2 ± 1.35]	[11,700 ± 680]	[46.0 ± 6.8]
$k^{CuL}{}_{H_2tetren}$	5.12 ± 0.67	2.76 ± 0.21]	3.59 ± 0.21
$k^{CuL}{}_{H_3tetren}$	0.04 ± 0.015	0.04 ± 0.010	

^{a} Previously reported[9] and included for comparison. ^{b} $k^{Cu(OH)L}{}_{Htetren}$ and $k^{CuL}{}_{tetren}$ or $k^{Cu(OH)L}{}_{H_2tetren}$ and $k^{CuL}{}_{Htetren}$ are alternative rate constants having the same hydrogen ion concentration dependence in the rate expression making them indistinguishable to the regression analysis. ^{c} Values × 10^{-3}. ^{d} Values × 10^{-6}.

Table III. Second-Order Rate Constants for the tetren Reaction with Cu(dien) in the Presence of Excess dien at pH 7.01, 25°, $\mu = 0.1$, $[\mathrm{Cu(dien)}]_0 = 1.00 \times 10^{-5}\ M$, and $[\mathrm{tetren}]_0 = 1.00 \times 10^{-5}\ M$

$10^4[\mathrm{dien}]_0, M$	$\epsilon_{\mathrm{initial}}$	$\epsilon_{\mathrm{equil}}$	$\Delta\epsilon^a$	$10^{-6}k^{\mathrm{Cu(dien)_t}}{}_{\mathrm{tetren_t}}$,[b] $M^{-1}\ \mathrm{sec}^{-1}$
0.0	934	2807	1873	0.270
0.0	1001	2807	1896	0.272
0.0	1001	2807	1806	0.270
				Av 0.270
1.00	773	2745	1972	0.297
1.00	773	2745	1972	0.291
	740	2745	2005	0.247
				Av 0.278
10.0	1268	2745	1477	0.346
10.0	1268	2745	1477	0.378
10.0	1268	2745	1477	0.369
				Av 0.364
100	3546	4846	1300	0.364
100	3546	4846	1300	0.376
100	3546	4846	1300	0.351
				Av 0.364

[a] λ 280 nm. [b] Equilibrium calculations predict $[\mathrm{Cu(dien)_2}]_0 < 2\%\ [\mathrm{Cu(dien)}]_0$ and $[\mathrm{Cu(tetren)}]_{\mathrm{equil}} > 94\%\ [\mathrm{Cu(dien)}]_0$ in the presence of the 1000-fold excess dien.

conditions and results are given in Table III. The value of $\Delta\epsilon$ used in calculating the second-order rate constant was calculated from the initial and equilibrium transmittance readings on the Polaroid pictures taken from the oscilloscope. The average least-squares values of the second-order rate constants of 2.70×10^5, 2.78×10^5, 3.64×10^5, and $3.64 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ for 0-, 10-, 100-, and 1000-fold excess dien, respectively, show an increase in the rate constant of only 1.3 in the presence of 100- and 1000-fold excess dien. This is not a dramatic change, and while the possibility exists that excess dien speeds the exchange reaction, it is not felt that this is conclusive evidence but certainly does show that excess dien does not slow the exchange reaction.

It has been hypothesized that the formation of the $\mathrm{Cu(dien)_2}$ complex might have significant rate-slowing effects on the exchange reactions as a result of the removal of labile solvent molecules as available sites for initial attack by the incoming tetren. This trend was not observed. The observed profiles of reactions 2 and 3 (Figure 3) overlap in the pH region where $\alpha_{\mathrm{Cu(dien)_2}}$ is significant indicating the rate-slowing effect of a second complexed dien is even less than the rate-slowing effect caused by the formation of $\mathrm{Cu(OH)dien^+}$. Such a small effect caused by excess dien is reasonable if one of the dien ligands in $\mathrm{Cu(dien)_2}$ is labile and not fully complexed. Such a postulate is reasonable in light of the stability constants for Cu(dien) and $\mathrm{Cu(dien)_2}$ which have been reported as $\log K^{\mathrm{Cu}}{}_{\mathrm{Cu(dien)}} = 15.82$ and $\log K^{\mathrm{Cu(dien)}}{}_{\mathrm{Cu(dien)_2}} = 5.20$.[5] This difference in the stability constants and comparisons of the heats of formation of the various polyamine complexes[17] indicate the formation of $\mathrm{Cu(dien)_2}$ involves the effective complexation of either four or five amine nitrogens. Copper's propensity for forming square-planar amine complexes with weakly bound axial groups has been amply demonstrated with ammonia and ethylenediamine.[11]

Determination of the Stability Constant for Cu(OH)trien. The formation constant for Cu(OH)trien had previously been reported as $\log K^{\mathrm{Cu(trien)}}{}_{\mathrm{Cu(OH)trien}} = 3.2$ at 25° in 0.1 F $\mathrm{KNO_3}$.[18] In this work a potentiometric titration of 3.0×10^{-2} F Cu(trien) with 2.5 F KOH (Figure 5) gives no indication of a buffer region near pH 10.8 as would be expected on the basis of the stability constant expression

$$K^{\mathrm{Cu(trien)}}{}_{\mathrm{Cu(OH)trien}} = \frac{[\mathrm{Cu(OH)trien}]}{[\mathrm{Cu(trien)}][\mathrm{OH}]}$$

and the corresponding buffer equation

$$\mathrm{p}K_{\mathrm{w}} - \mathrm{p}K^{\mathrm{Cu(trien)}}{}_{\mathrm{Cu(OH)trien}} = \mathrm{pH} + \log\frac{[\mathrm{Cu(OH)trien}]}{[\mathrm{Cu(trien)}]}$$

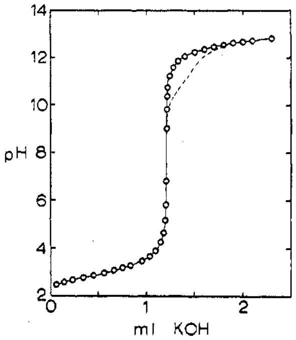

Figure 5. Potentiometric titration of ~25 ml of $3.0 \times 10^{-2}\ M$ Cu(trien) with 2.5 F KOH. The end point observed at ca. 1.2 ml corresponds to the titration of the protons contributed by the trien·$2\mathrm{H_2SO_4}$ used to prepare the solution. The dashed line corresponds to the curve that would be expected on the basis of the previously reported formation constant[18] of $k^{\mathrm{Cu(trien)}}{}_{\mathrm{Cu(OH)trien}} = 10^{3.2}$.

which would imply pH ~10.8 when [Cu(OH)trien] = [Cu(trien)].

The color of 3×10^{-4} F Cu(trien), prepared from stoichiometric volumes of copper nitrate and trien·$2\mathrm{H_2SO_4}$ solutions, changes from light purple (pH <12) to light blue (pH >12). Spectra (450–700 nm) as a function of pH (pH 8–13) were obtained using 4.78×10^{-3} F Cu(trien) prepared in the same way at 25° in 0.1 F $\mathrm{NaClO_4}$. The absorbance maximum decreased and shifted to longer wavelength with increasing pH ($A_{\max} = 0.730$ at 575 nm and pH 11, 0.530 at 650 nm and pH 13.4) with an isosbestic point observed at 640 nm. Figure 6 is a plot of the observed absorbance as a function of pH at 550 nm in a 1-cm cell. The spectrophotometric determination of $K^{\mathrm{Cu(trien)}}{}_{\mathrm{Cu(OH)trien}}$ is based on eq 11–13 where ϵ_{obsd} is the observed molar absorptivity, $\epsilon_{\mathrm{Cu(trien)}}$ and $\epsilon_{\mathrm{Cu(OH)trien}}$ are the molar absorptivities for Cu(trien) and Cu(OH)trien, and $f_{\mathrm{Cu(trien)}}$ and $f_{\mathrm{Cu(OH)trien}}$ are the fractions of Cu(trien) and Cu(OH)trien in solution.

$$f_{\mathrm{Cu(trien)}} + f_{\mathrm{Cu(OH)trien}} = 1 \tag{11}$$

$$\epsilon_{\mathrm{obsd}} = \epsilon_{\mathrm{Cu(trien)}}f_{\mathrm{Cu(trien)}} + \epsilon_{\mathrm{Cu(OH)trien}}f_{\mathrm{Cu(OH)trien}} = \epsilon_{\mathrm{Cu(trien)}}f_{\mathrm{Cu(trien)}} + \epsilon_{\mathrm{Cu(OH)trien}}(1 - f_{\mathrm{Cu(trien)}}) \tag{12}$$

$$K^{\mathrm{Cu(trien)}}{}_{\mathrm{Cu(OH)trien}} = \frac{[\mathrm{Cu(OH)trien}]}{[\mathrm{Cu(trien)}][\mathrm{OH}]} = \frac{f_{\mathrm{Cu(OH)trien}}}{f_{\mathrm{Cu(trien)}}[\mathrm{OH}]} = \frac{[1 - f_{\mathrm{Cu(trien)}}]}{f_{\mathrm{Cu(trien)}}[\mathrm{OH}]} \tag{13}$$

Table IV. Predicted Rate Constants (M^{-1} sec^{-1}) for Possible Rate-Determining Steps

Structure	$K^{Cu}{}_{Cu(trien)tetren}/K^{Cu}{}_{Cu(trien)}$[a]	To form	k_{rds}, sec^{-1}	$k^{Cu(trien)}{}_{tetren}$(predicted)
I	1	III	$k^{-N} = 100$	1.0×10^2
I	1	II	$k^{-H_2O} = 1.2 \times 10^7$	1.2×10^7
II	0.282	IV	$k^{-N} = 100$	2.8×10
III	5.13×10^{-5}	IV	$k^{-H_2O} = 1.2 \times 10^7$	6.15×10^2
IV	7.24×10^{-3}	VI	$k^{-H_2O} = 1.2 \times 10^7$	8.7×10^4
V	4.07×10^{-7}	VII	$k^{-N} = 100$	4.1×10^{-5}
VI	8.32	VII	$k^{-N} = 100$	8.3×10^2

[a] The value of $K^{Cu}{}_{Cu(trien)tetren}$ is estimated as follows for intermediates I–VI. The values of the stability constants used in these calculations are found in ref 1c or 2: (I) $K = K^{Cu}{}_{Cu(trien)} = 10^{20.1}$; (II) $K = K^{Cu}{}_{Cu(trien)}K_{Cu(NH_3)_5} = 10^{20.1-0.55} = 10^{19.55}$; (III) $K = K^{Cu}{}_{Cu(dien)} = 10^{15.81}$; (IV) $K = K^{Cu}{}_{Cu(dien)}K_{Cu(NH_3)_4} = 10^{15.81+2.15} = 10^{17.96}$; (V) $K = K^{Cu}{}_{Cu(en)}K_{Cu(NH_3)_3} = 10^{10.73+2.98} = 10^{13.71}$; (VI) $K = K^{Cu}{}_{Cu(dien)}K^{Cu(dien)}{}_{Cu(dien)_2} = 10^{15.81+5.21} = 10^{21.02}$.

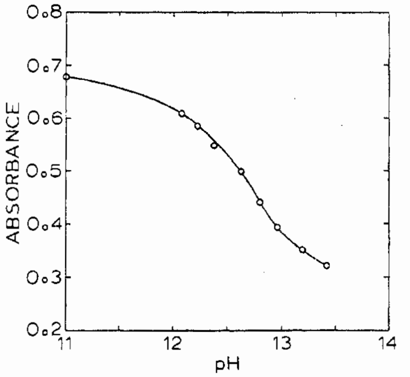

Figure 6. Absorbance observed as a function of pH (λ 550 nm, 25.0°, $\mu = 0.10\,M$ (NaClO$_4$), 1-cm cell) of 4.78×10^{-3} F Cu(trien) prepared from copper(II) nitrate and trien·2H$_2$SO$_4$ salts.

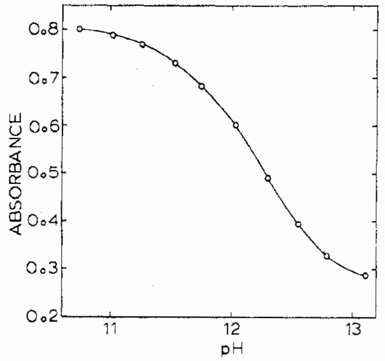

Figure 7. Absorbance observed as a function of pH (λ 270 nm, 25.0°, $\mu = 0.10\,M$ (NaClO$_4$), 1-cm cell) of 1.00×10^{-4} F Cu(dien) prepared from copper(II) nitrate and dien·HCl salts.

Dividing eq 11 by $f_{Cu(trien)}$ and solving for $1/f_{Cu(trien)}$ leads to eq 14. Rearrangement of eq 13 leads to eq 15. Equating eq 14 and 15 and making appropriate substitutions of the Beer–Lambert law (where the cell path length is 1 cm) and water dissociation expression results in eq 16 in which A_{obsd} represents the observed absorbance at a given pH and [Cu(trien)]$_t$ represents the total stoichiometric concentration of Cu(trien) complexes in solution.

$$1/f_{Cu(trien)} = [\epsilon_{Cu(trien)} - \epsilon_{Cu(OH)trien}]/[\epsilon_{Obsd} - \epsilon_{Cu(OH)trien}] \qquad (14)$$

$$1/f_{Cu(trien)} = K^{Cu(trien)}{}_{Cu(OH)trien}[OH] + 1 \qquad (15)$$

$$A_{obsd} = \epsilon_{Cu(OH)trien}[Cu(trien)]_t + \frac{[\epsilon_{Cu(trien)}[Cu(trien)]_t - A_{obsd}][H^+]}{K^{Cu(trien)}{}_{Cu(OH)trien}K_w} \qquad (16)$$

The formation constant was calculated from the least-squares slope of a straight-line plot of A_{obsd} vs. ($\epsilon_{Cu(trien)}$·[Cu(trien)]$_t$ − A_{obsd})[H$^+$]. The best value was found to be log $K^{Cu(trien)}{}_{Cu(OH)trien}$ = 1.2. This value was used in eq 10 for resolution of the independent rate constants. The formation of Cu(OH)trien at pH >12 is in good agreement with the pH profile of the reaction and is believed to be responsible for the decrease in the observed rate of exchange.

Determination of the Stability Constants for Cu(OH)dien and Cu(OH)$_2$dien. The formation constant for Cu(OH)dien has been variously reported to have a value of log $K^{Cu(dien)}{}_{Cu(OH)dien}$ = 4.5[8a] or 5.17[8b] at 25° in 0.1 F KNO$_3$. This formation constant was remeasured in this work at 25° in 0.1 F NaClO$_4$ by potentiometric titration of 0.2 F Cu(dien) with 15 F KOH. The best value for the formation constant was found to be log $K^{Cu(dien)}{}_{Cu(OH)dien}$ = 4.5; this value was used in the interpretation of the kinetic data.

At higher pH (>11) spectrophotometric evidence indicated the formation of a second species assumed to be Cu(OH)$_2$dien. Figure 7 is a plot of the observed absorbance as a function of pH for a 1.00×10^{-4} F Cu(dien) solution at 25° also 0.1 F in NaClO$_4$. The absorbances were measured using a 1-cm cell (λ 270 nm). An equation analogous to eq 16 was used to calculate the formation constant. The best value was found to be log $K^{Cu(OH)dien}{}_{Cu(OH)_2dien}$ = 1.93. This value was used in eq 10 for resolution of the independent rate constants for reaction 2. The formation of Cu(OH)dien and Cu(OH)$_2$dien is in good agreement with the observed pH profile of reaction 2 and these species are believed to be responsible for the decrease in the observed rate of exchange at high pH.

Discussion

Reaction of tetren with Cu(trien). The resolved rate constants for displacement of trien or tren by tetren are quite similar, the ratios of the rate constants $k^{Cu(trien)}{}_{tetren}/k^{Cu(tren)}{}_{tetren}$, $k^{Cu(trien)}{}_{H(tetren)}/k^{Cu(tren)}{}_{H(tetren)}$, $k^{Cu(trien)}{}_{H_2tetren}/k^{Cu(tren)}{}_{H_2tetren}$, $k^{Cu(trien)}{}_{H_3tetren}/k^{Cu(tren)}{}_{H_3tetren}$ being 1.4, 2.7, 0.54, 1.0, respectively. However, the ratio of the rate constants $k^{Cu(OH)trien}{}_{tetren}/k^{Cu(OH)tren}{}_{tetren}$ = 34 is comparatively large and provides evidence supporting the suggestions that Cu(OH)tren has a trigonal-bipyramidal structure with no labile solvent (H$_2$O) molecules in the inner coordination sphere while Cu(OH)trien retains an octahedral structure with one remaining inner-sphere solvent molecule providing a site for more rapid attack by the incoming tetren.

The similarity in the resolved rate constants $k^{CuL}{}_{tetren}$, $k^{CuL}{}_{Htetren}$, $k^{CuL}{}_{H_2tetren}$, and $k^{CuL}{}_{H_3tetren}$, where L = tren or trien, suggests that the displacement of trien by tetren can be submitted to the same mechanistic arguments previously applied in detail to the displacement of tren by trien.[9] Figure 8 shows the possible intermediates and microscopic reactions proposed for the displacement reactions. Table IV gives the

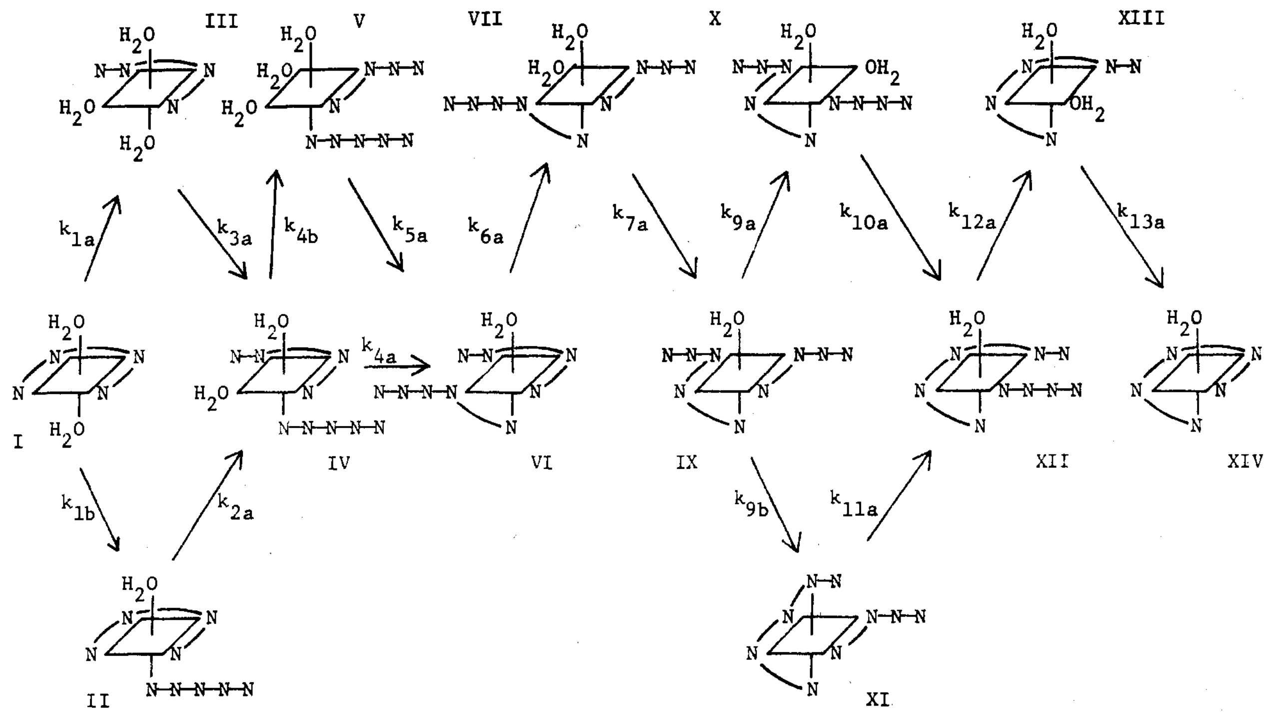

Figure 8. Possible intermediates and microscopic reactions proposed for the displacement of trien by tetren.

predicted rate constants for possible rate-determining steps based on the equation

$$k^{\mathrm{Cu(trien)}}{}_{\mathrm{tetren}} = k_{\mathrm{rds}}K^{\mathrm{Cu(tetren)}}{}_{\mathrm{Cu(trien)tetren}} = k_{\mathrm{rds}}\frac{K^{\mathrm{Cu}}{}_{\mathrm{Cu(trien)tetren}}}{K^{\mathrm{Cu}}{}_{\mathrm{Cu(trien)}}} \qquad (17)$$

where $k^{\mathrm{Cu(trien)}}{}_{\mathrm{tetren}}$ is the observed rate constant, k_{rds} is the rate constant for the rate-determining step, and $K^{\mathrm{Cu(tetren)}}{}_{\mathrm{Cu(trien)tetren}}$ is a stability constant equal to the ratio of the stability constants $K^{\mathrm{Cu}}{}_{\mathrm{Cu(trien)tetren}}/k^{\mathrm{Cu}}{}_{\mathrm{Cu(trien)}}$. Details regarding the mechanistic arguments have been discussed in ref 9 and can be applied directly by replacing Cu(tren) by Cu(trien) and trien by tetren. The most likely pathway to products is proposed to be I–II–IV–VI–VII–IX–X–XII–XIII–XIV (Figure 8) with water loss in step k_{4a} assumed to be rate determining on the basis of comparison between predicted and experimentally resolved values (Table IV). The analogous step was determined to be rate determining in the displacement of tren by tetren.[9] After the work with Cu(tren) was submitted for publication, Hunt et al.[19] reported a rate constant for water loss from $\mathrm{Cu(tren)^{2+}}$ as $k^{-\mathrm{H_2O}} = 2.5 \times 10^5$ $\mathrm{sec^{-1}}$ from $^{17}\mathrm{O}$ NMR experiments. When used to calculate a predicted rate constant for displacement of tren by trien, this value gives improved agreement between predicted (4.0×10^4 M^{-1} $\mathrm{sec^{-1}}$ instead of 2.9×10^5 M^{-1} $\mathrm{sec^{-1}}$) and experimentally resolved (5.4×10^4 M^{-1} $\mathrm{sec^{-1}}$) rate constants. The overall aspects of the mechanistic arguments remain unchanged.

The rate of water loss from $\mathrm{Cu(trien)^{2+}}$ has not been measured. However, Pearson and Lanier[20] have measured the rate of the exchange reaction of $\mathrm{Cu(en)_2{}^{2+}}$ with ethylenediamine as 1.8×10^6 M^{-1} $\mathrm{sec^{-1}}$ at 27° using NMR line-broadening techniques. They attribute their exchange to the rate of water loss from the inner coordination sphere of the complex. Assuming an Eigen mechanism,[21,22] the rate of water loss is estimated to be $k^{-\mathrm{H_2O}} = k_{\mathrm{obsd}}/K_{\mathrm{os}} = 1.8 \times 10^6$ M^{-1} $\mathrm{sec^{-1}}/0.15$ $M^{-1} = 1.2 \times 10^7$ $\mathrm{sec^{-1}}$. Since $\mathrm{Cu(en)_2{}^{2+}}$ and $\mathrm{Cu(trien)^{2+}}$ are expected to have similar square-planar structures, this value is used in calculating the predicted rate constant in Table IV. The predicted rate constant (8.7×10^4 M^{-1} $\mathrm{sec^{-1}}$) for step IV to VI agrees closely with the resolved value (7.5×10^4 M^{-1} $\mathrm{sec^{-1}}$). Thus the rate of water loss from IV is the probable rate-determining step. It is probable that the rate of water loss from species IV (k_{4a}) is not the same as from the parent complex (species I) but this assumption seems to be the best approximation available. (An alternative would be to assume that the rate of water loss from Cu(tren)tetren equals that from Cu(trien)tetren.)

Reactions of tetren with $\mathbf{Cu(dien)^{2+}}$ and $\mathbf{Cu(dien)_2{}^{2+}}$. The displacement of dien by tetren was found to be about 1000 times faster than displacement of trien, the ratios of the rate constants $k^{\mathrm{Cu(OH)dien}}{}_{\mathrm{tetren}}/k^{\mathrm{Cu(OH)_2(dien)}}{}_{\mathrm{tetren}}$, $k^{\mathrm{Cu(dien)}}{}_{\mathrm{tetren}}/k^{\mathrm{Cu(trien)}}{}_{\mathrm{tetren}}$, $k^{\mathrm{Cu(dien)}}{}_{\mathrm{Htetren}}/k^{\mathrm{Cu(trien)}}{}_{\mathrm{Htetren}}$, and $k^{\mathrm{Cu(dien)}}{}_{\mathrm{H_2tetren}}/k^{\mathrm{Cu(trien)}}{}_{\mathrm{H_2tetren}}$ being 770, 1365, 784, and 1300, respectively. The relative effect on the rate due to the $\mathrm{Cu(dien)^{2+}} \rightleftarrows \mathrm{Cu(OH)dien^{+}}$ or the tetren $\rightleftarrows$ $\mathrm{Htetren^{+}}$ equilibrium is comparable to analogous equilibria of other systems. The ratios of the rate constants $k^{\mathrm{Cu(trien)}}{}_{\mathrm{tetren}}/k^{\mathrm{Cu(OH)trien}}{}_{\mathrm{tetren}}$ and $k^{\mathrm{Cu(dien)}}{}_{\mathrm{tetren}}/k^{\mathrm{Cu(OH)dien}}{}_{\mathrm{tetren}}$ are 4.3 and 7.6, respectively, and $k^{\mathrm{Cu(trien)}}{}_{\mathrm{tetren}}/k^{\mathrm{Cu(trien)}}{}_{\mathrm{Htetren}}$, $k^{\mathrm{Cu(tren)}}{}_{\mathrm{tetren}}/k^{\mathrm{Cu(tren)}}{}_{\mathrm{Htetren}}$, and $k^{\mathrm{Cu(dien)}}{}_{\mathrm{tetren}}/k^{\mathrm{Cu(dien)}}{}_{\mathrm{Htetren}}$ are 2.5, 4.9,[9] and 4.4, respectively. These similarities in relative rate constants imply that the change in structure upon the conversion of Cu(dien) to Cu(OH)dien is similar to that for conversion of Cu(trien) to Cu(OH)trien but quite different from the conversion of Cu(tren) to Cu(OH)tren. Also, the effect of singly protonating the incoming tetren is the same for all species investigated.

The $\mathrm{Cu(OH)dien^{+}} \rightleftarrows \mathrm{Cu(OH)_2dien}$ equilibrium proposed from observations in this work is found to have an additional, more significant rate-slowing effect such that $k^{\mathrm{Cu(OH)dien}}{}_{\mathrm{tetren}}/k^{\mathrm{Cu(OH)_2dien}}{}_{\mathrm{tetren}} = 17$. The overall effect of the $\mathrm{Cu(dien)^{2+}} \rightleftarrows \mathrm{Cu(OH)_2dien}$ equilibrium is comparable to that of the $\mathrm{Cu(tren)^{2+}} \rightleftarrows \mathrm{Cu(OH)tren^{+}}$ system, the ratios $k^{\mathrm{Cu(dien)}}{}_{\mathrm{tetren}}/k^{\mathrm{Cu(OH)_2dien}}{}_{\mathrm{tetren}}$ and $k^{\mathrm{Cu(tren)}}{}_{\mathrm{tetren}}/k^{\mathrm{Cu(OH)tren}}{}_{\mathrm{tetren}}$ being 130 and 110, respectively. In both cases, two labile solvent sites are made unavailable to the incoming tetren by the formation of the hydroxy mixed complex. The additional implication is that $\mathrm{Cu(OH)_2dien}$ is a pentacoordinate trigonal bipyramid similar in structure to Cu(OH)tren. Since the tetren is uncharged, electrostatic differences due to changes in charge of the complex are not important and the 100-fold rate constant decrease must be due to the less rapid loss of hydroxide or chelated nitrogen from the copper complex.

The rate of attack of H_2tetren on $Cu(H_2O)_6^{2+}$ has been measured[23] to be 4.2 × 10^7 M^{-1} sec^{-1} and the value found for $k^{Cu(dien)}{}_{H_2tetren}$ = 3.6 × 10^6 M^{-1} sec^{-1} is only 1 order of magnitude slower. Since Cu(dien) has only two axial and one equatorial inner-sphere water molecules and also would be expected to be less affected than $Cu(H_2O)_6^{2+}$ by the ICB mechanism due to the decreased acidity of its coordinated water molecules, our conclusion is that polyamine substitution can begin on Cu(dien) without rupture of a copper–nitrogen coordinate bond. The rate-determining step then is the loss of the first water molecule from $Cu(dien)^{2+}$.

The rate of attack of unprotonated tetren on both aquocopper and $Cu(dien)^{2+}$ can be expected to be enhanced by the internal conjugate base (ICB) mechanism as described by Rorabacher.[22] This effect should be smaller for Cu(dien) however due to the lesser acidity of its coordinated water molecules compared to $Cu(H_2O)_6^{2+}$. If the rate of water loss calculated for $Cu(en)_2^{2+}$ is used (1.2 × 10^7 sec^{-1})[20] and the ICB mechanism is assumed to enhance the rate of water loss from $Cu(dien)^{2+}$ by a factor of 100, the rate predicted for the attack of tetren on $Cu(dien)^{2+}$ is given by $k^{Cu(dien)}{}_{tetren} = f_{ICB}k^{-H_2O}K_{os} = (100)(1.2 \times 10^7\ sec^{-1})(0.15\ M^{-1}) = 1.8 \times 10^8$ M^{-1} sec^{-1}, a value in good agreement with the resolved value of 1.02 × 10^8 M^{-1} sec^{-1} and differing from $k^{Cu}{}_{tetren}$ only by the extent to which the ICB mechanism differs for the two species. (The exchange of $Cu(en)_2^{2+}$ with ethylenediamine is not expected to undergo ICB enhancement since log $K^{Cu(en)_2}{}_{Cu(OH)(en)_2}$ is expected to be comparable to log $K^{Cu(trien)}{}_{Cu(OH)trien}$ = 1.2, too small to partake effectively in hydrogen bonding to a noncoordinated tetren molecule.)

The rate-determining step in the displacement of dien by unprotonated tetren is proposed to be the ICB-enhanced rate of water loss from the $Cu(dien)^{2+}$ complex. In comparison, the rate-determining step for displacement of trien or tren from copper by tetren appears to be the rate of water loss after the leaving ligand has freed one nitrogen to form a dien-like tridentate configuration.

No significant difference in the rate of attack of tetren on $Cu(dien)^{2+}$ or $Cu(dien)_2^{2+}$ could be observed. This is in sharp contrast to the rate-slowing effects observed when a second dien molecule is complexed with $Ni(dien)^{2+}$.[24] On the basis of such observations and the evidence cited earlier, one of the dien molecules in $Cu(dien)_2^{2+}$ might well be expected to behave more like ammonia (monodentate) or ethylenediamine (bidentate) and be similar in configuration and/or dissociative behavior. For comparison, Pearson and Lanier[20] reported the exchange limits for $Cu(NH_3)_4^{2+}$ with ammonia and for $Cu(NH_3)_5^{2+}$ with ammonia to be ≥1.9 × 10^7 M^{-1} sec^{-1} and >5.7 × 10^6 sec^{-1}, respectively, at 27°.

Registry No. tetren, 112-57-2; $Cu(trien)^{2+}$, 54468-55-2; $Cu(dien)^{2+}$, 55528-71-7; $Cu(dien)_2^{2+}$, 55493-55-5; $Cu(OH)trien^+$, 55528-72-8; $Cu(OH)dien^+$, 55493-56-6; $Cu(OH)_2dien$, 55493-57-7.

Supplementary Material Available. Tables V–VIII, showing individual values of k_{obsd} and pertinent experimental parameters, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC40654V-9-75.

References and Notes

(1) (a) The following abbreviations are used throughout this paper: en, enthylenediamine; dien, diethylenetriamine; trien, triethylenetetramine; tetren, tetraethylenepentamine; tren, tris(2-aminoethyl)amine. (b) The following pK_a values for the ligands are used throughout this paper: dien,[2] 9.94, 9.13, 4.34; trien,[3] 9.92, 9.20, 6.67, 3.32; tetren,[3] 10.00, 9.20, 8.20, 4.10, 2.60; tren,[4] 10.13, 9.43, 8.40. (c) The following formation constants are used throughout this paper: log $K^{Cu(dien)}{}_{Cu(dien)_2}$, 5.20;[5] log $K^{Cu}{}_{CuL}$, 15.80, 20.1, and 22.77 for L = dien,[5] trien,[6] and tetren,[7] respectively; log $K^{CuL}{}_{Cu(OH)L}$, 4.5 and 1.2 for L = dien and trien, respectively.
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(17) Heats of formation (kcal/mol) of copper complexes at 25° and 0.1 *M* ionic strength (KCl or KNO_3), assembled from ref 2 are as follows; the value listed in parentheses is the ΔH per bonding nitrogen atom: Cu(en), −13.0 (−6.50); $Cu(en)_2$, −25.4 (−6.35); Cu(dien), −18.0 (−6.00); $Cu(dien)_2$, −26.1 or −25.2; Cu(trien), −21.4 (−5.35); Cu(tren), −20.40 (−5.10); Cu(tetren), −24.95 (−4.99). Applying the range of values of $\Delta H/n$ to the case of $Cu(dien)_2$ shows 4.0–5.2 nitrogen atoms complexed.
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