ordering in the transition state is expected in the former case.

In summary, our results indicate that both associative and dissociative activation processes operate in the solvolysis reactions of $Pd(Et_4dien)X^+$ substrates. Apparently the steric requirements for effective associative activation are so severe that only small solvent molecules (or ligands) with accessible donor atoms qualify. This conclusion is consistent with the observation[1] that in aqueous solution only the powerful nucleophilic ligand $S_2O_3^{2-}$, which possesses an exposed sulfur donor atom $(-S^-)$, is able to utilize effectively a direct associative pathway. For all other entering groups the substitution rates are controlled by the associative solvolysis path to give an aquo intermediate.

Acknowledgments.—We thank the National Science Foundation for support of this research and the Stiftung für Stipendien auf dem Gebiete der Chemie, Switzerland, for a fellowship to R. R. during 1967.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEBRASKA,
LINCOLN, NEBRASKA 68508

Polyamine Substitution Reactions of Tris(2-aminoethyl)aminecopper(II)[1]

BY JAMES D. CARR* AND JOHN VASILIADES

Received January 14, 1972

The rates of the ligand-exchange reactions of dien, trien, and tetren with Cu(tren) are measured using stopped-flow spectrophotometry. The pH dependence of the reaction rate is analyzed and two unprotonated nitrogen donor atoms on the incoming ligand are sufficient for the displacement of tren. The rate constants for the attack of the unprotonated polyamine on Cu(tren) are 106×10^3, 85.2×10^3, and 54.1×10^3 for dien, trien, and tetren, respectively, at 25° and 0.1 *M* ionic strength. A mechanism is proposed wherein one nitrogen on the incoming ligand is bonded prior to the rate-determining step.

Introduction

The ligand-exchange reactions of tris(2-aminoethyl)-aminecopper(II) (abbreviated Cu(tren) or CuTr)[2]

$$\mathrm{Cu(tren)} + 2\mathrm{dien} \longrightarrow \mathrm{Cu(dien)_2} + \mathrm{tren} \tag{1}$$

$$\mathrm{Cu(tren)} + \mathrm{trien} \longrightarrow \mathrm{Cu(trien)} + \mathrm{tren} \tag{2}$$

$$\mathrm{Cu(tren)} + \mathrm{tetren} \longrightarrow \mathrm{Cu(tetren)} + \mathrm{tren} \tag{3}$$

with dien, trien, and tetren have been investigated. The Cu(tren) complex can exist in solution at high pH with a hydroxide ion coordinated to the copper ion in a ternary complex (abbreviated Cu(OH)tren). Cu(tren) has been reported to be a *cis*-diaquo octahedral[3a] structure while Cu(OH)tren exists as a trigonal-bipyramidal complex.[3b,c] Cu(trien), characterized as *trans*-diaquo octahedral,[4,5] is thermodynamically more stable than Cu(tren) due to the tetragonal distortion of the latter complex induced by the ligand structure. A planar arrangement of dentates is preferred by copper(II) to any nonplanar geometry. Reactions 1–3 are therefore favored to completion in the 6–12 pH range. Reactions 1–3 are rapid and are monitored by stopped-flow spectrophotometry. Many multidentate ligand replacement reactions have been reported in the literature but ligand-exchange kinetics of all-polyamine multidentate ligand systems have not been reported previously.

Experimental Section

A standard copper nitrate solution was prepared from pure metal and was standardized electrogravimetrically. This standard solution was used to standardize tren and tetren spectrophotometrically and to prepare Cu(tren). Cu(tren) was prepared by the addition of a slight excess of copper nitrate to a known quantity of ligand followed by precipitation of the excess as the metal hydroxide.

tren was obtained commercially from Jefferson Chemical Co. The liquid, gas chromatographically pure by the observation of only a single peak (20% SE-30 on silanized Chromosorb W, 190°, flow rate 20 ml/min), was dissolved in water and standardized by a mole ratio plot with the standard copper. trien was commercially obtained as the sulfate salt and was recrystallized according to the procedure of Reilley.[6] dien was recrystallized as the hydrochloride salt from a commercially obtained liquid.[7] tetren was precipitated as the sulfate salt from the impure commercial material obtained from Aldrich Chemical Co. and recrystallized according to the procedure of Reilley.[6]

A 0.01 *M* potassium borate–boric acid buffer system was used to control the pH of the solution. The large excess of free attacking ligand also served to buffer the solution. Solution pH was measured immediately after each kinetic run. Potassium nitrate was used to control the ionic strength at a value of 0.10 *M*. See Table I for reaction conditions.

Reactions 1–3 were followed spectrophotometrically in a 2-cm cell on a Durrum–Gibson stop-flow apparatus thermostated at $25 \pm 0.01°$. The photomultiplier signal was amplified and opposed by a voltage from a mercury battery source so that a selected portion of the per cent transmittance could be observed on a Tektronix 564 storage oscilloscope. (The 80–100% transmittance range was used for all the studies.) The stored image was photographed on Polaroid film. Reaction 2 was followed at the maximum absorption of Cu(trien) at 575 mμ (ε 150), under a variety of concentration ratios and levels including equal initial concentrations and with 10- and 20-fold excesses of trien to give pseudo-first-order reactions. All of these conditions were used to establish the pH profile (Figure 2) from pH 6.90 to 11.50. The excellent agreement of the rate constants observed

---

[1] This paper was presented in part at the Midwest Regional Meeting of the American Chemical Society, Kansas City, Mo., Nov 1969, and was abstracted from the thesis presented by J. V. to the University of Nebraska for the Ph.D. degree.

[2] The following abbreviations are used throughout this paper: tren, tris(2-aminoethyl)amine (Tr); trien, triethylenetetramine (T); tetren, tetraethylenepentamine (Te); dien, diethylenetriamine (D). All charges have been left out for convenience.

[3] (a) P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963); (b) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); (c) P. Paoletti and M. Ciampolini, *Ric. Sci., Suppl.*, **33** (IIA), 405 (1963).

[4] C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 887 (1956).

[5] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 5115 (1961).

[6] C. N. Reilley and A. Vavoulis, *Anal. Chem.*, **31**, 243 (1959).

[7] H. B. Jonassen, R. B. LeBlanc, A. W. Meibohm, and R. M. Rogan, *J. Amer. Chem. Soc.*, **72**, 2430 (1950).

TABLE I

REACTION CONDITIONS USED FOR THE RATE STUDIES OF POLYAMINES WITH Cu(tren) AT 25° AND $\mu = 0.1\ M$

Polyamine	[Polyamine]$_i$, M	[Cu(tren)]$_i$, M	pH
dien	3.23×10^{-2}	3.45×10^{-4}	7–12
	7.0×10^{-3}	3.45×10^{-4}	7–12
trien	1.84×10^{-4}[a]	1.84×10^{-3}	10.45
	1.49×10^{-2}	2.98×10^{-4}	10.58[b]
	5.96×10^{-3}	2.98×10^{-4}	10.77[b]
	2.98×10^{-3}	2.98×10^{-4}	7–11
	2.98×10^{-4}	2.98×10^{-4}	9.8–11.7
tetren	3.00×10^{-3}	3.00×10^{-4}	7–11

[a] $\mu = 0.05$. [b] $\lambda = 829$ nm.

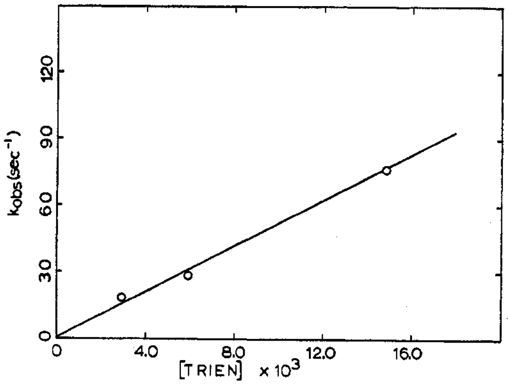

Figure 1.—Dependence of the pseudo-first-order rate constant on concentraton of the excess trien. [CuTr] = $2.98 \times 10^{-3}\ M$ (pH 10.7, $\mu = 0.10$, 25°.)

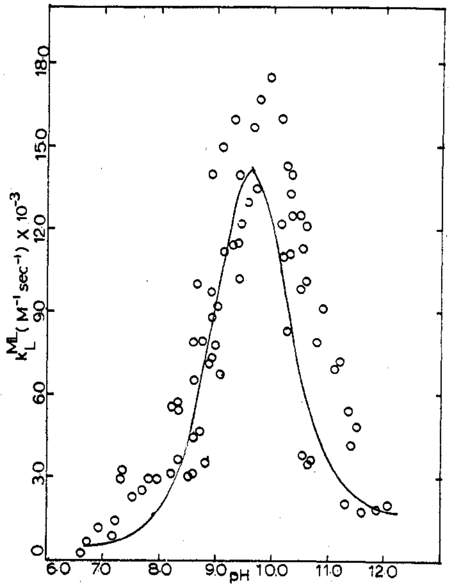

Figure 2.—Rate constant–pH profile for the reaction of dien with Cu(tren) at 25°, $\mu = 0.10$. Curves are calculated from the resolved rate constants of Table II.

in the different concentration situations shows that reaction 2 is first order in each reactant and second order overall throughout the pH range studied. The exchange reaction of Cu(tren) with tetren (reaction 3) was run under pseudo-first-order conditions with 10-fold excess ligand over Cu(tren) and followed at the absorption maximum of Cu(tetren) at 600 nm (ϵ 170). The exchange of Cu(tren) with dien (reaction 1) was followed at the maximum absorption of Cu(tren) at 830 nm (ϵ 117) using 20- and 100-fold excesses of dien over Cu(tren). The 20-fold or greater excess of ligand is needed since the reaction is thermodynamically favored to completion to form the bis complex but unfavored to form the mono Cu(dien) complex.

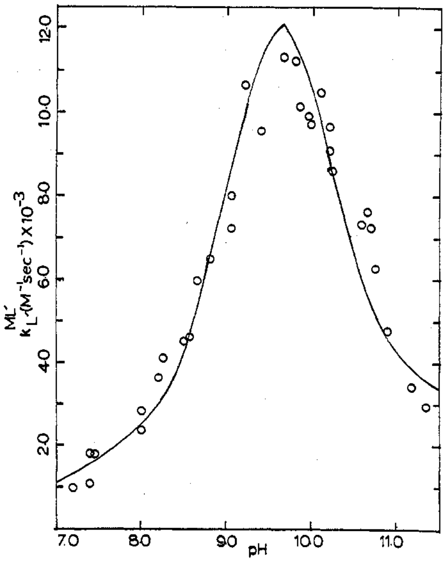

Figure 3.—Rate constant–pH profile for the reaction of trien with Cu(tren) at 25°, $\mu = 0.10$. Curves are calculated from the resolved rate constants of Table II.

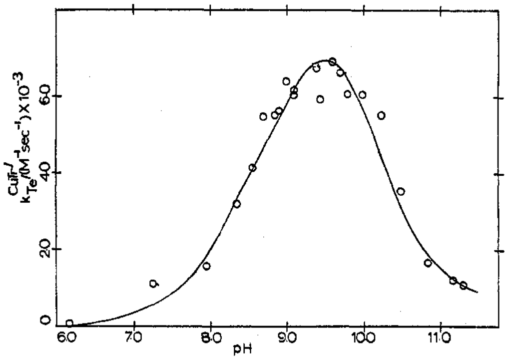

Figure 4.—Rate constant–pH profile for the reaction of tetren with Cu(tren) at 25°, $\mu = 0.10$. Curves are calculated from the resolved rate constants of Table II.

Excellent pseudo-first-order plots were obtained from the traces of reactions 1–3. A first-order program on the IBM 360 was used to calculate the slopes of these plots for which at constant pH

$$\text{rate} = -\frac{d[\text{CuTr}]}{dt} = k_{\text{obsd}}[\text{CuTr}]_T = k_{L_T}{}^{\text{CuTr}_T}[L]_T[\text{CuTr}]_T \quad (4)$$

The value of the observed first-order rate constant k_{obsd} is linearly dependent on the concentration of free ligand (Figure 1). A plot of $k_{L_T}{}^{\text{CuTr}_T}$ *vs.* pH was made to obtain the individual pH profiles (Figures 2–4). The subscript "T" implies the total or analytical concentration of all forms of the species involved.

The forward rate constants of reactions 1–3 were resolved into individual proton-dependent terms to fit the equation

$$k_{L_T}{}^{\text{CuTr}_T}[L]_T[\text{CuTr}]_T = k_L{}^{\text{CuOHTr}}[L][\text{CuOHTr}^+] + k_L{}^{\text{CuTr}}[L][\text{CuTr}^{2+}] + k_{HL}{}^{\text{CuTr}}[HL^+][\text{CuTr}^{2+}] + k_{H_2L}{}^{\text{CuTr}}[H_2L^{2+}][\text{CuTr}^{2+}] + k_{H_3L}{}^{\text{CuTr}}[H_3L^{3+}][\text{CuTr}^{2+}] \quad (5)$$

The pK_a values for the ligands used in the rate constant resolution are as follows: dien,[8] 9.94, 9.13, 4.34; trien,[9] 9.92, 9.20, 6.67, 3.32; tetren,[10] 10.0, 9.2, 8.2, 4.1; $K_w = 1.08 \times 10^{-14}$.

---

(8) J. E. Prue and G. Swartzenbach, *Helv. Chim. Acta,* **33,** 985 (1950).

(9) G. Swartzenbach, *ibid.,* **33,** 974 (1950).

(10) C. N. Reilley and J. H. Holloway, *J. Amer. Chem. Soc.,* **80,** 2917 (1958).

These calculations were performed with an IBM 360 computer using a weighted regression analysis program. Weighting of the data was necessary because the standard deviation of the observed rate constant is not constant. The weighting factor $1/Z^2$ was used in the regression analysis in order to give a statistical agreement with the relative experimental error of the rate constants which is approximately constant throughout the pH range

$$Z = k_{\mathrm{L_T}}{}^{\mathrm{CuTr_T}}\left(1 + \frac{[\mathrm{H}^+]}{K_{\mathrm{HL}}} + \frac{[\mathrm{H}^+]^2}{K_{\mathrm{HL}}K_{\mathrm{H_2L}}} + \frac{[\mathrm{H}^+]^3}{K_{\mathrm{HL}}K_{\mathrm{H_2L}}K_{\mathrm{H_3L}}}\right)\left(1 + \frac{K_{\mathrm{f}}K_{\mathrm{w}}}{[\mathrm{H}^+]}\right) = k_{\mathrm{L}}{}^{\mathrm{Cu(OH)Tr}}\frac{K_{\mathrm{f}}K_{\mathrm{w}}}{[\mathrm{H}^+]} + k_{\mathrm{L}}{}^{\mathrm{CuTr}} + k_{\mathrm{HL}}{}^{\mathrm{CuTr}}\frac{[\mathrm{H}^+]}{K_{\mathrm{HL}}} + k_{\mathrm{H_2L}}{}^{\mathrm{CuTr}}\frac{[\mathrm{H}^+]^2}{K_{\mathrm{HL}}K_{\mathrm{H_2L}}} + k_{\mathrm{H_3L}}{}^{\mathrm{CuTr}}\frac{[\mathrm{H}^+]^3}{K_{\mathrm{HL}}K_{\mathrm{H_2L}}K_{\mathrm{H_3L}}} \qquad (6)$$

Results

The reactions of dien, trien, and tetren with Cu(tren) were shown to be first order in polyamine and first order in the copper complex. The general expression in terms of total concentration of polyamine and Cu(tren) is given by eq 4.

Figures 2–4 show that the observed second-order rate constants for the dien, trien, and tetren reactions with Cu(tren) increase with increasing pH up to pH 9.6 and then decrease at still higher pH values. The reaction of dien with Cu(tren) is first order in dien where the observed rate constant results from eq 7 being rate limiting. A large excess of ligand is needed

$$\mathrm{Cu(tren) + dien \longrightarrow Cu(dien) + tren} \qquad (7)$$

$$\mathrm{Cu(dien) + dien \longrightarrow Cu(dien)_2} \qquad (8)$$

to drive reaction 1 to completion since reaction 7 is not thermodynamically favored to completion.[11] It is assumed that reaction 8 is very rapid.

The pH dependence of the rate constants can be expressed in terms of the various protonated polyamine species present in solution. The resolved rate constants are shown in Table II. The solid curves in the pH profiles are based on these resolved rate constants and eq 5. In reactions 1 and 2 only the first four terms of eq 5 contribute to the rate expression while in reaction 3 all five terms contribute to the expression. The second ($k_{\mathrm{L}}{}^{\mathrm{CuTr}}$) and third ($k_{\mathrm{HL}}{}^{\mathrm{CuTr}}$) terms in eq 6 can alternatively be expressed as the mono- and diprotonated ligand attack on Cu(OH)tren since the regression analysis cannot distinguish between the two rate expressions. These alternate terms are calculated and are included in Table II. The fit of the predicted curve is not as good at high pH for dien as for trien or tetren. We suspect only the experimental difficulty in measurement of these very rapid reactions as being responsible.

TABLE II

RESOLVED RATE CONSTANTS ($\times 10^{-3}$) FOR REACTIONS 1–3[a]

	Ligand		
	dien	trien	tetren
$k_{\mathrm{L}}{}^{\mathrm{CuOHTr}}$	1.70 ± 0.40	2.88 ± 0.42	0.51 ± 0.18
$k_{\mathrm{L}}{}^{\mathrm{CuTr}}$	106 ± 14.2 (7)	85.2 ± 8.4 (8)	54.1 ± 6.9 (9)
Or alternatively			
$k_{\mathrm{HL}}{}^{\mathrm{CuOHTr}}$	26.8 ± 3.60	22.8 ± 2.30	35 ± 4.5
$k_{\mathrm{HL}}{}^{\mathrm{CuTr}}$	20.9 ± 2.7 (6)	19.2 ± 2.3 (7)	11.1 ± 0.67 (8)
Or alternatively			
$k_{\mathrm{H_2L}}{}^{\mathrm{CuOHTr}}$	34.6 ± 4.5	27.1 ± 3.20	22.2 ± 1.35
$k_{\mathrm{H_2L}}{}^{\mathrm{CuTr}}$	0.425 ± 0.098 (5)	1.50 ± 0.12 (6)	5.12 ± 0.67 (7)
$k_{\mathrm{H_3L}}{}^{\mathrm{CuTr}}$			0.04 ± 0.015 (6)

[a] The number in parentheses following the rate constant value is the number of unprotonated nitrogen atoms available.

Discussion

The reaction of dien in displacing tren from copper is faster than that of trien which is faster than that of tetren. In general, two unprotonated nitrogen donor atoms on the incoming ligand are sufficient for the displacement of tren and although additional nitrogen atoms make the reaction more favorable thermodynamically, they make it less favorable kinetically.

It is found that increased protonation of the entering polyamine ligand slows the exchange reaction. This is reminiscent of the behavior of these same polyamines in substituting copper complexes of aminocarboxylates.[12] In that work it is suggested that a proton will rapidly situate itself in the intermediate prior to the rate-determining step on the most basic ligand site which is not coordinated to the metal ion. A proton on the entering ligand at the rate-determining step will slow an exchange reaction and one on the leaving ligand will speed up such a reaction. That increased protonation slows these reactions is evidence of their being on the entering ligand at the time of the rate-determining step and hence that this step comes early in the sequence before many nitrogen atoms of the leaving ligand have been freed. At high pH (pH >9.6) the rate decreases. This is attributed to a slower reaction of incoming unprotonated ligand with Cu(OH)Tr than with CuTr. The incoming ligand in this case must either displace a hydroxide ion or nitrogen group which is more difficult than the displacement of a solvent molecule. The trigonal-bipyramidal structure proposed[3] for Cu(OH)Tr leaves no coordinated solvent to be replaced by an incoming polyamine. This is contrasted to the *cis*-diaquo octahedral configuration of the species without a hydroxide ion which has two water molecules available.

The total number of nitrogen atoms available on an individual intermediate species is the 4 tren nitrogens plus the number, M, of nitrogen atoms in the attacking ligand: 5 for tetren, 4 for trien, and 3 for dien, or $4 + M$ total nitrogen atoms. The number of nitrogens capable of coordinating to copper is this number minus the number of hydrogen ions involved in the particular intermediate.

Comparisons of the resolved rate constants in Table II show that when the total number of unprotonated nitrogen atoms in the intermediate is 6 or fewer, there is no reaction or it is very slow compared to reactions in which 7 or more unprotonated nitrogens are available. The apparent exception to this is dien which still reacts at an appreciable rate when monoprotonated although only 6 unprotonated nitrogens are available in $k_{\mathrm{HD}}{}^{\mathrm{CuTr}}$. The ratio of the rate constants for $k_{\mathrm{D}}{}^{\mathrm{CuTr}}/k_{\mathrm{HD}}{}^{\mathrm{CuTr}} = 5.1$ and is very similar to the ratio of $k_{\mathrm{D}}{}^{\mathrm{CuCy}}/k_{\mathrm{HD}}{}^{\mathrm{CuCy}} = 15/3.4 = 4.4$.[13] The behavior of dien in that previous

---

(11) Stability constants for the different complexes at 25° and 0.1 M ionic strength: CuTr, log K = 18.8; CuT, log K = 20.1; CuTe, log K = 22.9; CuD, log K = 15.8; $\mathrm{CuD_2}$, log K = 5.22; Cu(OH)Tr, log K_{f} = 4.65. See L. G. Sillén and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17** (1964).

(12) R. E. Shepherd, G. M. Hodgson, and Dale W. Margerum, *Inorg. Chem.*, **10**, 989 (1971).

(13) J. D. Carr, R. A. Libby, and D. W. Margerum, *ibid.*, **6**, 1083 (1967).

work was also anomalous. A possible explanation is that the proposed intermediate prior to the rate-determining step (structure IV) would for dien present a much better chance of transferring the proton to the uncoordinated nitrogen of tren and not slow the reaction so greatly.

If the number of unprotonated nitrogen atoms is greater than 6, there is a less pronounced decrease in the rate constants with protonation. The differences in the rates of $k_{H_2L}^{CuTr}$ for trien and tetren can probably be attributed to the manner in which the incoming ligand is protonated.[14] Diprotonated trien is protonated on the first and third or first and fourth nitrogen atoms making it more difficult for the ligand to attack Cu(tren) in comparison to diprotonated tetren which always has two neighboring unprotonated nitrogens. Rorabacher and Turan have shown[15] that a primary amine nitrogen is much faster than a secondary nitrogen to substitute water in complex formation but that a protonated primary nitrogen is much slower to undergo such a reaction than an unprotonated one.

From the reaction order it may be inferred that the intermediate of these systems involves two polyamines, one breaking one bond at a time with its place being taken by a water molecule and the other forming one bond at a time displacing the water molecule until substitution is complete. Such a sequence has been reported in numerous other ligand-exchange reactions. Examination of the possible sequences of intermediates shows structures with one, two, or three water molecules coordinated in the primary coordination sphere. One can therefore propose intermediates as in Figure 5 provided that the following criteria are observed: (a) there can never be more than five nitrogen atoms coordinated to the copper ion (Bjerrum and Nielson have shown that copper can coordinate with three ethylenediamines but the third en group is bonded only with one nitrogen; the same authors measured this stability constant to be 0.10[16]); (b) the incoming ligand coordinates sequentially with one nitrogen atom at a time beginning with a terminal nitrogen; (c) intermediates with three or more water molecules in the first coordination sphere are of low stability in comparison to the starting complex; (d) there must be at least two unprotonated amine groups on the incoming ligand for the reaction to proceed at a reasonable rate; (e) any protons remain associated with the entering ligand at the rate-determining step since increased protonation is observed to slow rather than to speed the exchange; (f) when two reaction possibilities are available, the more rapid will occur.

The observed rate constant of such a reaction is related to the rate constant of the rate-determining step and the stability of the intermediate as follows

$$k_{L}^{CuTr} = k_{rds}K_{LCuTr}^{CuL} = \frac{k_{rds}K_{LCuTr}^{Cu}}{K_{CuTr}^{Cu}} \qquad (9)$$

If values of K_{LCuTr}^{Cu} can be estimated and k_{rds} assigned for a variety of choices, a predicted value of k_L^{CuTr} may be calculated. Discovery of a mechanism for which the predicted value agrees reasonably well with the observed value will be evidence for selecting such a mechanism as correct over any other possibilities. The approach taken is to estimate values of K_{LCuTr}^{Cu} using intermediate IV, for example, as the product of $K_{Cu(D)}$ and $K_{Cu(NH_3)_4}$ where $K_{Cu(NH_3)_4}$ is the fourth ammonia stability constant. Values for the different intermediates are listed in Table III, as K_{LCuTr}^{Cu}. Electrostatics have little effect on these estimates since we are dealing with neutral ligands.

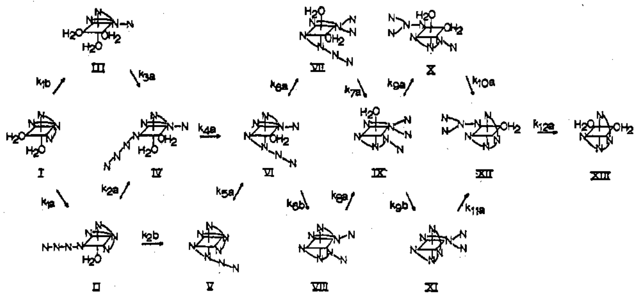

Figure 5.—Possible intermediates and microscopic reactions leading to displacement of tren.

TABLE III

VALUES OF PREDICTED RATE CONSTANTS (M^{-1} sec^{-1}) FOR POSSIBLE RATE-DETERMINING STEPS

Structure	$K_{TCuTr}^{Cu\,a}/K_{CuTr}^{Cu}$	To form	k_{rds}, sec^{-1}	k_T^{CuTr} (predicted)
I	1	III	$k^{-N} = 100$	1.0×10^2
I	1	II	$k^{-H_2O} = 1.8 \times 10^6$	1.8×10^6
II	2.82×10^{-1}	IV	$k^{-N} = 100$	2.8×10^1
II	2.82×10^{-1}	V	$k^{-H_2O} = 1.8 \times 10^6$	5.1×10^5
III	1.0×10^{-3}	IV	$k^{-H_2O} = 1.8 \times 10^6$	1.8×10^3
IV	1.58×10^{-1}	VI	$k^{-H_2O} = 1.8 \times 10^6$	2.9×10^5
V	1.0×10^{-1}	VI	$k^{-N} = 100$	1.0×10^1
VI	1.58×10^2	VII	$k^{-N} = 100$	1.6×10^4

[a] The value of K_{TCuTr}^{Cu} is estimated as follows for intermediates I–VI. The values of the stability constants used in these calculations are found in ref 11. (I) $K = K_{CuTr}^{Cu} = 10^{18.8}$; (II) $K = K_{CuTr}^{Cu} \times K_{Cu(NH_3)_5} = 10^{18.8-0.55} = 10^{18.25}$; (III) $K = K_{CuD}^{Cu} = 10^{15.8}$; (IV) $K = K_{CuD}^{Cu} \times K_{Cu(NH_3)_4}^{Cu} = 10^{15.8+2.19} = 10^{18.0}$; (V) $K = K_{CuTr}^{Cu} \times K_{Cu(en)_3}^{Cu} = 10^{18.8-1.0} = 10^{17.8}$; (VI) $K = K_{CuD}^{Cu} \times K_{CuD_2}^{CuD} = 10^{15.8+5.2} = 10^{21.0}$.

Wilkins has measured the rate constant for the breakage of the first copper–nitrogen bond in $Cu(en)_2$ as 4.43 sec^{-1} at 0.8°.[17] The same author reported the breakage of the copper–nitrogen bond in Cu(en) as 115 sec^{-1} at 25° with $E = 13$ kcal.

Pearson and Lanier, using nmr line-broadening techniques, have measured the rate of the exchange reaction of $Cu(en)_2$ with ethylenediamine as 1.8×10^6 M^{-1} sec^{-1} at 27°.[18] They attributed their exchange to the rate of water loss from the inner coordination sphere of the complex. Margerum, *et al.*,[19] have shown that the rate of bond rupture of water or ammonia from nickel depends strongly on the nature of other ligands coordinated to the nickel ion. One must therefore be very careful in making a choice of such rate constants for the intermediates of unknown structures in this study and realize the approximate nature of such calculations.

In Figure 5 a choice first must be made for the correct branch of the predominant reaction pathway to form structures IV, VI, IX, and XII. Step k_{1b} does not add stability to the complex intermediate and is unfavorable

---

[14] J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1698 (1964).

[15] T. S. Turan and D. B. Rorabacher, private communication.

[16] J. Bjerrum and E. J. Nielsen, *Acta Chem. Scand.*, **2**, 297 (1948).

[17] R. G. Wilkins, *J. Chem. Soc.*, 4475 (1962).

[18] R. G. Pearson and R. D. Lanier, *J. Amer. Chem. Soc.*, **86**, 765 (1964).

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

since it involves breaking a copper–nitrogen bond, but k_{3a} is favorable because of the addition of a fourth nitrogen group. Step k_{1a} involves the addition of a nitrogen to the complex making it thermodynamically more stable than I. Therefore I to II is more likely than I to III. Step k_{2b} involves the coordination of a sixth N group on copper which makes it very unstable thermodynamically.[16] Therefore a more likely path is II–IV–VI rather than II–V–VI. Structures VIII and XI can also be disregarded since they involve a six-nitrogen-coordinated complex. The most likely pathway to products therefore seems to be I–II–IV–VI–VII–IX–X–XII–XIII. From the kinetic results we know that the rate-determining step must occur quite early in the reaction path.[20] Application of eq 9 to the microscopic reactions shown in this sequence shows that the predicted rate constant agrees quite closely with the observed value for step IV to VI and that the rate of water loss from IV to VI is the probable rate-determining step.

The possibility exists that the intermediate may be converting from octahedral to trigonal bipyramidal. Such a conversion may occur and still be consistent with our interpretation of the data since, in both cases—the octahedral and bipyramidal structures—the number of bonded nitrogens would be the same as would the rate-determining step. The only difference would be in the number of inner coordinated water molecules.

In continuation of our work the ligand-exchange reaction of Cu(tren) + trien is used as a propagating step in the double ligand-exchange reactions of Cu(tren) + Zn(trien). Such coordination reactions have been used for trace metal analysis.[21] By using an all-polyamine coordination chain, a built-in selectivity for analysis of transition metals in the presence of alkaline earths is afforded.

Acknowledgment.—Financial assistance from National Science Foundation Departmental Science Development Grant No. NSF-GU-2054 is gratefully acknowledged.

---

(20) Tables of the individual values of k_{obsd} and pertinent experimental parameters will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-2104. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(21) D. W. Margerum and R. K. Steinhaus, *Anal. Chem.*, **37**, 222 (1965)

CONTRIBUTION FROM THE INSTITUTE OF CHEMISTRY,
THE HEBREW UNIVERSITY, JERUSALEM, ISRAEL

Thermochemistry of Lanthanide Complexes in the Thenoyltrifluoroacetone–Bipyridyl System

BY A. S. KERTES* AND E. F. KASSIERER

Received January 11, 1972

The stepwise equilibrium constants, enthalpy, entropy, and free energy changes for the addition of 2,2′-bipyridyl to some tris(thenoyltrifluoroacetonato)lanthanide(III) chelates have been determined by direct titration calorimetry in chloroform solution at 25°. The metal diketonates accept up to two molecules of the base; the stepwise heats and entropies of addition depend on the ionic radii of the lanthanides (La, Nd, Gd, and Lu). The adducts are stabilized by the large exothermic enthalpy changes.

It has been known for some years that many neutral tris(β-diketonato)lanthanide(III) chelates easily accommodate extra donor groups of a variety of oxygen- or nitrogen-containing bases, yielding stable crystalline solids.[1-8] In all these compounds, with a stoichiometry Ln:diketone:base of 1:3:1, the lanthanides exhibit octacoordinate properties. There is a variety of spectral evidence[4,9-11] that all these Lewis bases complex directly to the central cation. The diketones occupy six coordination sites around the lanthanide atom; thus the base molecule, if bound in addition, will raise the coordination number above six, rather than one or more diketone oxygens being displaced. In instances in which the coordinated donors are water molecules,[5,9,12-16] the tris diketonates may have a hydration number as high as three, the dihydrate being the most stable.

There is enough evidence[17] that such mixed-ligand adducts of lanthanides are of considerable stability in solution of organic solvents of low polarity. There is

---

(1) L. L. Smith, USAEC Report DP-913, 1964.

(2) E. Butter and K. Kreher, *Wiss. Z. Karl-Marx-Univ. Leipzig*, **14**, 881 (1965).

(3) J. E. Schwarberg, D. R. Geve, R. E. Sievers, and K. J. Eisentraut, *Inorg. Chem.*, **6**, 1933 (1967).

(4) R. C. Ohlmann and R. G. Charles, *J. Chem. Phys.*, **40**, 3131 (1964).

(5) M. F. Richardson, W. F. Wagner, and D. E. Sands, *J. Inorg. Nucl. Chem.*, **30**, 1275 (1968).

(6) L. I. Kononenko, M. A. Tishchenko, R. A. Vitkun, and N. S. Poluektov, *Russ. J. Inorg. Chem.*, **10**, 1341 (1965).

(7) E. V. Melenteva, L. I. Kononenko, and N. S. Poluektov, *ibid.*, **11**, 200 (1966).

(8) J. Selbin, N. Ahmad, and N. Bhacca, *Inorg. Chem.*, **10**, 1383 (1971).

(9) R. G. Charles and R. C. Ohlmann, *J. Inorg. Nucl. Chem.*, **27**, 255 (1965).

(10) F. Halverson, J. S. Brinen, and J. R. Leto, *J. Chem. Phys.*, **41**, 157 (1964).

(11) J. R. Ferraro, L. J. Basile, and D. L. Kovacic, *Inorg. Chem.*, **5**, 391 (1966).

(12) G. W. Pope, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **20**, 304 (1961).

(13) M. A. Gouveia, M. de Jesus Tavares, and R. G. de Carvahlo, *ibid.*, **33**, 817 (1971).

(14) J. A. Cunningham, D. E. Sands, and W. F. Wagner, *Inorg. Chem.*, **6**, 499 (1967).

(15) M. A. Bhaumik and M. L. El-Sayed, *J. Phys. Chem.*, **69**, 275 (1965).

(16) M. L. Morris, R. W. Moshier, and R. E. Sievers, *Inorg. Chem.*, **2**, 411 (1963).

(17) A. S. Kertes in "Recent Advances in Liquid-Liquid Extraction," C. Hanson, Ed., Pergamon Press, Oxford, 1970, p 16; Y. Marcus and A. S. Kertes, "Ion Exchange and Solvent Extraction of Metal Complexes," Wiley-Interscience, London, 1969, Chapter 11.