Figure 4. Plot of the basicity constant of the complex against the $[M(3,2,3\text{-tet})]^{2+}$ stability constant.

three metal ions. If we assume that the formation of the protonated complex involves the equilibrium $[M(3,2,3\text{-tet})]^{2+} + H^+ \rightleftarrows [MH(3,2,3\text{-tet})]^{3+}$, we notice that the basicity of the complex varies in the order $Zn^{2+} > Ni^{2+} > Cu^{2+}$ which is the reverse of the Irving–Williams order found for the 1:1 complexes. Plotting the basicity constant defined in this way as ordinate and the stability constant for the complex $[M(3,2,3\text{-tet})]^{2+}$ as abscissa we obtain a straight-line relationship (Figure 4). As a consequence we can assume (1) the protonation of the nitrogen involves the same process for all three complexes, (2) the inverse proportionality between the constants of protonation and of complex formation provides evidence that the attachment of a proton involves the opening of a chelate ring, and (3) the stereochemistry of these complexes both in the protonated and in the nonprotonated forms does not vary with the metal ion, even if the problem of the type and the number of isomers remains unsolved. It is worthwhile that the Zn^{2+} ion forms with this ligand an octahedral complex in aqueous solution.

Table IV. Stability constants of Nickel(II), Copper(II), and Zinc(II) Complexes of Linear Aliphatic Polyamines

Effect of Adding a Six-Membered Ring to a Five-Membered Ring

$[Ni en]^{2+}$ [a]	$[Ni(2,3\text{-tri})]^{2+}$ [b]	$[Ni(3,2,3\text{-tet})]^{2+}$
7.70	11.23	14.69
└───── 3.53 ─────┘ └ 3.46 ─────┘		

$[Cu en]^{2+}$ [a]	$[Cu(2,3\text{-tri})]^{2+}$ [b]	$[Cu(3,2,3\text{-tet})]^{2+}$
10.58	16.60	21.83
└───── 6.02 ─────┘ └ 5.17 ─────┘		

$[Zn en]^{2+}$ [a]	$[Zn(2,3\text{-tri})]^{2+}$ [b]	$[Zn(3,2,3\text{-tet})]^{2+}$
5.79	8.77	11.26
└───── 2.98 ─────┘ └ 2.49 ─────┘		

Effect of Adding a Five-Membered Ring to a Six-Membered Ring

$[Ni tn]^{2+}$ [c]	$[Ni(2,3\text{-tri})]^{2+}$ [b]	$[Ni(2,3,2\text{-tet})]^{2+}$ [d]
6.91	11.23	16.4
└───── 4.32 ─────┘ └ 5.53 ─────┘		

$[Cu tn]^{2+}$ [c]	$[Cu(2,3\text{-tri})]^{2+}$ [b]	$[Cu(2,3,2\text{-tet})]^{2+}$ [d]
10.16	16.60	23.9
└───── 6.44 ─────┘ └ 7.30 ─────┘		

[a] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 4553 (1960). [b] Reference 17. [c] F. Holmes and R. Williams, *J. Chem. Soc. A*, 1702 (1967). [d] Reference 1.

Let us consider the relative stability constants for Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes with ligands of varying denticity (Table IV). Going from $[Men]^{2+}$ to $[M(2,3\text{-tri})]^{2+}$ and from $[M(2,3\text{-tri})]^{2+}$ to $[M(3,2,3\text{-tet})]^{2+}$ involves in both cases the addition of a six-membered ring, in the first case to a simple five-membered ring and in the second case to a five-membered ring attached to a six-membered ring. The differences between the stability constants indicate that this linking has a greater stabilizing effect in the first case. The opposite occurs when we consider the addition of a five-membered ring to an isolated six-membered ring tn^{22} or to one linked to another five-membered ring 2,3-tri. Thus it would appear that the effect of the increased degree of crowding in the two cases is different, in one case facilitating the ability of the ligand to coordinate and in the other hindering it.

Substitution Reactions of Sterically Hindered Gold(III) Complexes

DAVID L. FANT and C. F. WEICK*

The complexes $[Au(Me_2dien\text{-}H)Cl]PF_6$, $[Au(Me_4dien\text{-}H)Cl]PF_6$, and $[Au(Et_2dien\text{-}H)Cl]PF_6{}^1$ have been synthesized and the dissociation constants of their conjugate acids measured. Kinetic studies reveal that the complexes containing the methylated ligands undergo bromide substitution by the usual two-path mechanism common to low-spin d^8 metal complexes. Substitution of $[Au(Et_2dien\text{-}H)Cl]^+$ is postulated to proceed *via* a ring-opening mechanism.

Introduction

Square-planar metal complexes generally undergo substitu-

tion at rates that are reagent dependent.[2] In particular such dependence has been observed for substitution by monoden-

(1) Abbreviations used in this paper: amine, any diethylenetriamine or substituted diethylenetriamine; amine-H, the conjugate base of amine; dien, $NH_2CH_2CH_2NHCH_2CH_2NH_2$; dien-H, $(NH_2CH_2CH_2NCH_2CH_2NH_2)^-$; Me_2dien, $(CH_3)_2NCH_2CH_2NHCH_2CH_2NH_2$; Me_2-dien-H, $[(CH_3)_2NCH_2CH_2NCH_2CH_2NH_2]^-$; Me_4dien, $(CH_3)_2NCH_2$-$CH_2NHCH_2CH_2N(CH_3)_2$; Me_4dien-H, $[(CH_3)_2NCH_2CH_2NCH_2CH_2N$-$(CH_3)_2]^-$; Et_2dien, $(C_2H_5)_2NCH_2CH_2NHCH_2CH_2NH_2$; Et_2dien-H, $[(C_2H_5)_2NCH_2CH_2NCH_2CH_2NH_2]^-$; Et_4dien, $(C_2H_5)_2NCH_2CH_2$-$NHCH_2CH_2N(C_2H_5)_2$; Et_4dien-H, $[(C_2H_5)_2NCH_2CH_2NCH_2CH_2N$-$(C_2H_5)_2]^-$; Me_5dien, $(CH_3)_2NCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)_2$; $MeEt_4$dien, $(C_2H_5)_2NCH_2CH_2N(CH_3)CH_2CH_2N(C_2H_5)_2$.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 5.

tate ligands in diethylenetriamine complexes of Pt(II),[3,4] Pd(II),[4,5] and Au(III).[6] However, certain *N*-alkyl-substituted diethylenetriamine complexes of these metals react at rates that are almost independent of the concentration of the entering reagent.[7-10] Such complexes have alkyl groups which occupy the regions above and below the plane of the ion. It has been suggested that these groups inhibit reagent attack.

The reaction studied in this investigation is the replacement of chloride by bromide in complexes of the type [Au(amine-H)Cl]⁺. Rate data for the reactions at 25° of [Au(dien-H)-Cl]⁺ [6] and [Au(Et₄dien-H)Cl]⁺ [9] have been reported. Since these two ions represent extremes in alkyl substitution, it was reasonable to expect other alkyl-substituted diethylenetriamine complexes of Au(III) to react at measurable rates.

Experimental Section

Materials. Fine gold powder of better than 99.99% purity was obtained from Alfa Inorganics Inc. The *N*-alkyl-substituted diethylenetriamines were used as purchased from Ames Laboratories Inc. All other chemicals used were reagent grade.

Analyses. Gold analyses were performed by dissolving a small amount of the complex in aqua regia followed by repeated evaporation with concentrated HCl to remove volatile oxides of nitrogen. The solutions of HAuCl₄ thus obtained were diluted to a final concentration of approximately 10^{-4} M. The absorbance of these solutions was measured at 314 nm using a Beckman DK-2 spectrophotometer. The gold concentration was then read from a previously prepared standard curve of absorbance *vs.* concentration of HAuCl₄.

The chloride content of [Au(Et₂dien-H)Cl]PF₆ was determined by the Mohr method.[11]

Preparation of Complexes. Solutions of tetrachloroauric acid were prepared as stated above. When the volume was reduced to 1-2 ml, the solution was allowed to cool and hydrated crystals of tetrachloroauric acid formed.

[Au(Et₂dien-H)Cl]PF₆. HAuCl₄·xH₂O equivalent to 1 g of gold was dissolved in 5 ml of ice-cold ether. This was added dropwise with stirring to a solution containing 5 ml of 1,1-diethyldiethylenetriamine in 15 ml of ice-cold ether. Throughout the addition of the HAuCl₄, the reaction mixture was maintained at a temperature of less than 5°.

An orange grease or paste formed during the addition of the HAuCl₄. The ether was decanted and the paste washed with three 10-ml portions of ice-cold ether. The paste was then dissolved in 15 ml of iced water and extracted with ten 30-ml portions of ice-cold ether. One gram of NH₄PF₆ was added and the aqueous solution allowed to freeze in a Dry Ice–acetone bath. The frozen mixture was then allowed to thaw under running water with vigorous agitation. The resulting red crystals were collected and recrystallized from ethanol, washed successively with ethanol and ether, and dried. The product was stored in a refrigerator at a temperature below 10°. A yield of 32% (based on the weight of gold) was obtained. *Anal.* Calcd for [Au(Et₂dien-H)Cl]PF₆: Au, 36.8; Cl, 6.6. Found: Au, 36.5; Cl, 6.7.

[Au(Me₂dien-H)Cl]PF₆. The procedure used for the preparation of [Au(Me₂dien-H)Cl]PF₆ was similar to that employed for [Au(Et₂dien-H)Cl]PF₆ but crystallization did not occur when the frozen mixture was allowed to thaw. An additional 1.5 g of NH₄PF₆ was added and the freeze and thaw procedure repeated without success. Finally the mixture was evaporated under reduced pressure. When the volume of the solution was reduced to half of its original volume, bright red crystals formed. These were collected on filter paper, recrystallized from ethanol, and dried in a desiccator over CaCl₂. The yield was 25% (based on the weight of gold used). *Anal.* Calcd for [Au(Me₂-dien-H)Cl]PF₆: Au, 38.6. Found: Au, 38.6.

(3) H. B. Gray, *J. Amer. Chem. Soc.*, **84**, 1548 (1962).

(4) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Amer. Chem. Soc.*, **82**, 4200 (1960).

(5) J. S. Coe and J. R. Lyons, *J. Chem. Soc. A*, 2669 (1969).

(6) W. H. Baddley and F. Basolo, *Inorg. Chem.*, **3**, 1087 (1964).

(7) W. H. Baddley and F. Basolo, *J. Amer. Chem. Soc.*, **86**, 2075 (1964).

(8) W. H. Baddley and F. Basolo, *J. Amer. Chem. Soc.*, **88**, 2944 (1966).

(9) C. F. Weick and F. Basolo, *Inorg. Chem.*, **5**, 576 (1966).

(10) J. B. Goddard and F. Basolo, *Inorg. Chem.*, **7**, 936 (1968).

(11) "Standard Methods for the Examination of Water, Sewage and Industrial Wastes," 10th ed, American Public Health Association, New York, N. Y., 1955, p. 60.

Table I. Absorption Maxima and Extinction Coefficients

Complex ion	ν_1, nm	Log ϵ_1	ν_2, nm	Log ϵ_2
[Au(Me₂dien-H)Cl]⁺	380	3.19	262	3.49
[Au(Me₂dien-H)Br]⁺	390	3.26	292	3.36
[Au(Me₂dien-H)OH]⁺	358	3.16		
[Au(Me₂dien)Cl]²⁺	310	3.02		
[Au(Et₂dien-H)Cl]⁺	382	3.19	260	3.52
[Au(Et₂dien-H)Br]⁺	396	3.26	295	3.38
[Au(Et₂dien-H)OH]⁺	364	3.16		
[Au(Et₂dien)Cl]²⁺	313	3.08		
[Au(Me₄dien-H)Cl]⁺	398	3.17		
[Au(Me₄dien-H)Br]⁺	412	3.23		
[Au(Me₄dien-H)OH]⁺	367	3.12		
[Au(Me₄dien)Cl]²⁺	366	3.30		

[Au(Me₄dien-H)Cl]PF₆. This compound was prepared in the same manner as the [Au(Et₂dien-H)Cl]PF₆. The red crystals were recrystallized from a solution of 70% ethanol in acetone, washed with absolute alcohol, and dried over CaCl₂. A yield of 33% (based on the weight of gold used) was obtained. *Anal.* Calcd for [Au(Me₄-dien-H)Cl]PF₆: Au, 36.6. Found: Au, 36.8.

Spectrophotometric Measurements. Ultraviolet absorption spectra for the complexes encountered in this work were obtained using a Perkin-Elmer Model 202 spectrophotometer. Data on absorption maxima and extinction coefficients are presented in Table I.

Equilibria Studies. Previous studies of the aqueous solution chemistry of [Au(dien-H)Cl]⁺ [12] and [Au(Et₄dien-H)Cl]⁺ [9] had indicated that (a) these complexes undergo extensive hydrolysis in neutral aqueous solution, (b) an excess of halide ion represses hydrolysis of these complexes within certain pH ranges, (c) the conjugate acids of these complexes are stable in perchloric acid, and (d) the conjugate acid of [Au(Et₄dien-H)Cl]⁺ undergoes decomposition in hydrohalic acids.

Spectral studies of aqueous solutions of the complexes isolated in the present work indicated that these, too, are hydrolyzed in 0.5 M NaClO₄ yielding equilibrium mixtures of [Au(amine-H)Cl]⁺ and [Au(amine-H)OH]⁺. The pH range over which this hydrolysis can be repressed by excess chloride and bromide ion was determined by the following procedure.

A portion of each of the complexes was dissolved in a small volume of water and the resulting solution was adjusted to pH >9.5 with 1 M NaOH. Each solution was passed down a Dowex 1-X8 anion-exchange column in the hydroxide form to convert the complex to the [Au(amine-H)OH]⁺ species. The effluent from the column was collected in a volumetric flask. Sufficient solid NaCl or NaBr was added to produce a halide ion concentration of 0.5 M on dilution to the mark.

Each solution was placed in a jacketed beaker and maintained at 25.0 ± 0.1°. The spectrum of aliquots of each solution was obtained as the pH was decreased in small increments using HClO₄. These studies indicate that within the pH range of 5.5–7.5 the complexes are completely in the form [Au(amine-H)Cl]⁺ in 0.5 M Cl⁻ and [Au-(amine-H)Br]⁺ in 0.5 M Br⁻.

Acid Dissociation Constants. The absorption spectra of solutions of [Au(Me₂dien-H)Cl]PF₆ and [Au(Me₄dien-H)Cl]PF₆ in 0.5 M Cl⁻ over the pH range 7.0–1.5 were obtained in the same manner as for the base hydrolysis measurements. Isosbestic points were observed at 263, 302, and 336 nm for [Au(Me₂dien-H)Cl]PF₆ and at 347 nm for [Au(Me₄dien-H)Cl]PF₆. Absorption of the acetone added to the latter solution (concentration 1%) to enhance solubility prevented observation of isosbestic points below 300 nm.

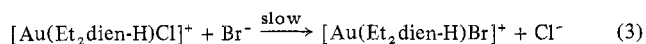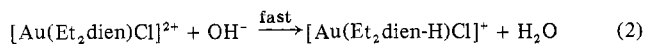Equilibrium constants for reaction 1 (where amine = Me₂dien

$$[\text{Au(amine)Cl}]^{2+} \overset{K_a}{\rightleftarrows} [\text{Au(amine-H)Cl}]^+ + \text{H}^+ \tag{1}$$
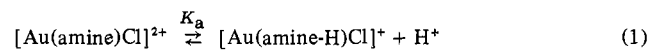
and Me₄dien) were obtained from absorbance values at 380 nm. A study of spectral changes occurring in a solution of [Au(Et₂dien-H)-Cl]PF₆ in 0.5 M Cl⁻ produced no isosbestic points. In the presence of high chloride ion concentration this complex began to decompose to AuCl₄⁻ below pH 4. Observation of the spectral changes occurring in 0.5 M ClO₄⁻ revealed the acid form of the complex to be stable in this medium but showed evidence of hydrolysis at pH values greater than 3.0. However spectral studies in mixed NaCl–NaClO₄ media (μ = 0.5) revealed that hydrolysis could be sufficiently repressed to allow determination of the acid dissociation constant of this com-

(12) W. H. Baddley, F. Basolo, H. B. Gray, C. Notting, and A. J. Poe, *Inorg. Chem.*, **2**, 921 (1963).

plex. Absorbance values at 367 nm were used for this computation.

Kinetic Studies. Solutions of each complex containing either 0.5 M Cl$^-$ or 0.5 M Br$^-$ were prepared in pH 6.8 phosphate buffers. From the spectra of these solutions wavelengths of 310 nm for [Au(Et$_2$dien-H)Cl]$^+$ and [Au(Me$_2$dien-H)Cl]$^+$ and 330 nm for [Au(Me$_4$dien-H)Cl]$^+$ were selected for the kinetic studies.

Solutions of the conjugate acid of [Au(amine-H)Cl]PF$_6$ were prepared in 0.04 M HClO$_4$. In each kinetic run this solution was allowed to react with an equal volume of a bromide ion solution which also contained sufficient phosphate buffer and NaClO$_4$ to produce, after mixing, a pH of 6.8 and an ionic strength of 0.115. The reaction sequence of [Au(Et$_2$dien-H)Cl]PF$_6$ is

$$[Au(Et_2dien)Cl]^{2+} + OH^- \xrightarrow{\text{fast}} [Au(Et_2dien-H)Cl]^+ + H_2O \quad (2)$$

$$[Au(Et_2dien-H)Cl]^+ + Br^- \xrightarrow{\text{slow}} [Au(Et_2dien-H)Br]^+ + Cl^- \quad (3)$$

Rates were determined using an Aminco-Morrow stopped-flow apparatus in conjunction with the monochromator from a Beckman DU spectrophotometer, an Aminco kinetic photometer, a Tetronix 531 oscilloscope, and a Polaroid oscilloscope camera.

All reactions were performed at a temperature of $25.0 \pm 0.1°$. The concentration of the complex in each case was 4×10^{-4} M. For all complexes, bromide concentrations of 0.05, 0.01, and 0.005 M were used. Additionally, [Au(Et$_2$dien-H)Cl]$^+$ was studied at 0.001 M. For each complex, replicate runs were performed at each concentration level. Reproducibility was better than 1% transmittance.

Absorbance values were obtained from the photographs of the oscilloscope trace and pseudo-first-order rate constants computed from the slope of plots of log $(A_\infty - A_t)$ vs. t. Plots of replicate runs yielded slopes which agreed within 10%.

Results and Discussion

Acid Dissociation Constants. The acid dissociation constants obtained in this study are presented in Table II along with those previously reported for [Au(dien)Cl]$^{2+}$ and [Au-(Et$_4$dien)Cl]$^{2+}$. The much higher acidity of the tetraethyl derivative, [Au(Et$_4$dien)Cl]$^{2+}$, relative to the unsubstituted complex, [Au(dien)Cl]$^{2+}$, has been attributed to solvation effects.[9] The more positive acid is more solvated than its conjugate base for both the alkyl-substituted and unsubstituted complexes. However this difference is smaller for the substituted complex because of its larger size. This results in a higher acidity for the alkyl-substituted ion. The pK_a values presented in Table II support this explanation in that increasing acidity parallels increasing alkyl substitution.

The essentially equal acidities of the isomeric ions [Au-(Et$_2$dien)Cl]$^{2+}$ and [Au(Me$_4$dien)Cl]$^{2+}$ are of special interest. Molecular models of these ions suggest that the two ethyl groups are more effective in shielding the central Au(III) from the bulk solvent than are the four methyl groups. Thus a previous suggestion[9] that the weak acidity of [Au-(dien)Cl]$^{2+}$ could be attributed to a weak coordination of solvent molecules along the z axis accompanied by a reduction in the effective positive charge on Au(III) is not supported by these results. If such solvent coordination did occur, [Au(Et$_2$dien)Cl]$^{2+}$ might be expected to be a much stronger acid than [Au(Me$_4$dien)Cl]$^{2+}$.

The relative stabilities of these acidic complexes in the presence of various anions deserves special comment. All are stable in 1 M perchloric acid but only the complexes containing coordinated dien, Me$_2$dien, and Me$_4$dien are stable in 1 M acidic chloride and bromide solutions. The complexes containing Et$_2$dien and Et$_4$dien break up in acidic chloride and bromide solutions, to yield AuCl$_4^-$ and AuBr$_4^-$, respectively. Thus in acidic solution the presence of ethyl groups on the terminal nitrogens of the chelate exerts a specific effect leading to ring opening. This effect is apparently not operative when the terminal nitrogens are methylated.

Kinetic Studies. The rate data obtained in this study are presented in Table III. Figures 1 and 2 illustrate the linear

Table II. Acid Dissociation Constants of
N-Alkyl-Substituted Diethylenetriaminegold(III) Complexes
(25°; $\mu = 0.50$ with NaCl)

Complex	pK_a	Complex	pK_a
[Au(dien)Cl]Cl$_2$	4.7^a	[Au(Et$_2$dien)Cl]PF$_6$	3.6^b
[Au(Me$_2$dien)Cl]PF$_6$	4.2	[Au(Et$_4$dien)Cl]PF$_6$	2.2^{b,c}
[Au(Me$_4$dien)Cl]PF$_6$	3.8		

^{a} Taken from ref 6. ^{b} μ adjusted to 0.50 with NaCl + NaClO$_4$. ^{c} Taken from ref 9.

Table III. Pseudo-First-Order Rate Constants at 25°
(pH 6.8) for the Reaction ($\mu = 0.115^a$)

$$[Au(amine-H)Cl]^+ + Br^- \xrightarrow{H_2O} [Au(amine-H)Br]^+ + Cl^-$$

amine-H = Me$_2$dien-H		amine-H = Me$_4$dien-H		amine-H = Et$_2$dien-H	
[Br$^-$], M	k_{obsd}, sec^{-1}	[Br$^-$], M	k_{obsd}, sec^{-1}	[Br$^-$], M	k_{obsd}, sec^{-1}
0.050	2.4	0.050	0.10	0.050	0.21
0.010	0.69	0.010	0.070	0.010	0.065
0.005	0.41	0.005	0.066	0.005	0.044
				0.001	0.023

^{a} Ionic strength adjusted with phosphate buffer and NaClO$_4$.

relationship between the pseudo-first-order rate constants and the bromide ion concentration for each complex and indicate that these reactions follow the rate law

$$\text{rate} = k_s[\text{complex}] + k_{Br}[\text{complex}][Br^-] \quad (4)$$

The slopes, k_{Br}, and intercepts, k_s, of these lines are listed in Table IV together with similar results previously obtained for [Au(dien-H)Cl]$^+$ and [Au(Et$_4$dien-H)Cl]$^+$.

For the latter two complexes the usual two-path bimolecular mechanism was assumed to be operative. Thus k_{Br} was considered to be the rate constant for a direct displacement of chloride by bromide while k_s represented the rate constant for solvent-assisted displacement. The very small rate constant values for [Au(Et$_4$dien-H)Cl]$^+$ were attributed to steric effects.[9] Similar steric retardation of square-planar substitution reactions has been reported by other authors for complexes of the types [Pd(amine)Cl]$^+$ (amine = Et$_4$dien, Me$_3$-dien, MeEt$_4$dien)[8,10] and [Pt(Et$_4$dien)Cl]$^+$.[13]

If this two-path mechanism is operative for all of the reactions whose rate constants are presented in Table IV, the reaction rates should decrease with increasing shielding of the Au(III) by the alkyl groups on the amine ligand. Examination of molecular models indicates that this shielding increases in the order dien-H < Me$_2$dien-H < Me$_4$dien-H < Et$_2$dien-H ≪ Et$_4$dien-H.

It is apparent from Table IV that the solvent path follows this predicted order. However, an anomaly is apparent in the reaction rates for the bromide path in that [Au(Et$_2$dien-H)Cl]$^+$ reacts 5 times faster than [Au(Me$_4$dien-H)Cl]$^+$.

Direct substitution of chloride by bromide involves an attack by a negatively charged bromide ion. Substitution *via* the solvent path, however, involves attack by a neutral water molecule. Thus the anomalously high rate for direct bromide ion substitution in [Au(Et$_2$dien-H)Cl]$^+$ could be rationalized if the effective positive charge at the central gold atom in this ion were higher than the corresponding charge in [Au(Me$_4$dien-H)Cl]$^+$. Such a variation in charge density might conceivably arise from inductive effects, solvation effects, or some combination of both. However, the acid dissociation constants do not support such an explanation. As stated above a higher positive charge on the central atom in

(13) R. Wango, Masters Thesis, Northwestern University, Evanston, Ill., 1964.

Table IV. First-Order and Second-Order Rate Constants for the Reactions of [Au(amine-H)Cl]$^+$ with Bromide Ion in Water (pH 6.8) at 25°

Complex	k_s, sec^{-1}	k_{Br}, M^{-1} sec^{-1}
[Au(dien-H)Cl]$^{+ a}$	0.6	90
[Au(Me$_2$dien-H)Cl]$^+$	0.20	44
[Au(Me$_4$dien-H)Cl]$^+$	0.062	0.76
[Au(Et$_2$dien-H)Cl]$^+$	0.023	3.8
[Au(Et$_4$dien-H)Cl]$^{+ b}$	0.00012	0.0085^c

^{a} Taken from ref 6. ^{b} Taken from ref 9. ^{c} Obtained from the slope of a plot of k_{obsd} *vs.* [Br$^-$] from Table I of ref 9.
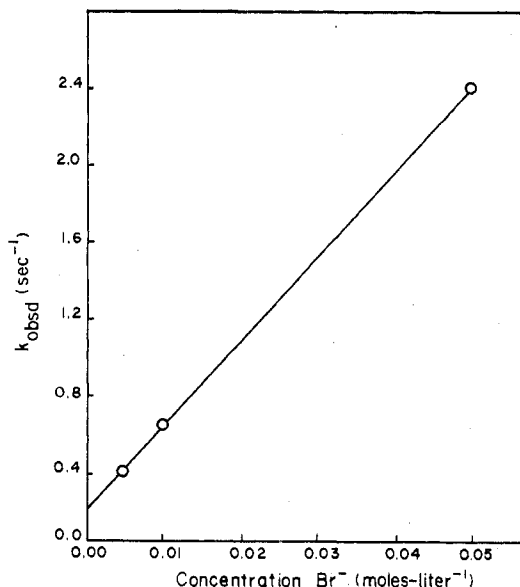
Figure 1. Dependence of k_{obsd} on the concentration of bromide ion for the reaction of [Au(Me$_2$dien-H)Cl]$^+$ with this reagent.

[Au(Et$_2$dien)Cl]$^{2+}$ should result in a lower pK_a for this complex relative to the pK_a of [Au(Me$_4$dien)Cl]$^{2+}$. The fact that the pK_a values for these two ions are essentially identical invalidates the above hypothesis.

The relative stabilities of these two complexes in the presence of high halide ion concentrations suggests a reasonable explanation for the results of the kinetic studies. As previously stated, the presence of ethyl groups on the terminal nitrogens of the chelate ligand leads to ring opening on acidification of the solution. This behavior suggests that these complexes are in equilibrium with low concentrations of ions containing the triamine as a bidentate ligand. These "open ring" ions are more susceptible to attack. Thus bromide substitution in these complexes can proceed by the mechanism

(5)
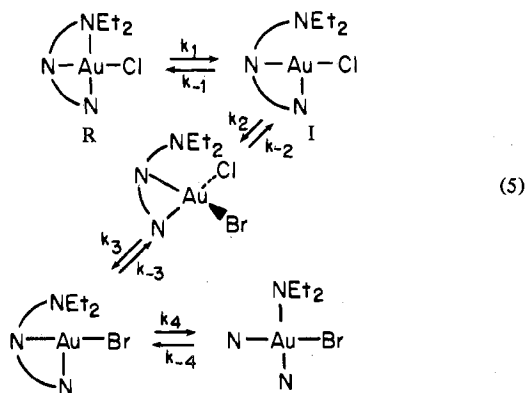
Under the experimental conditions used in this study (*i.e.*, high bromide ion concentration) the reaction goes to comple-
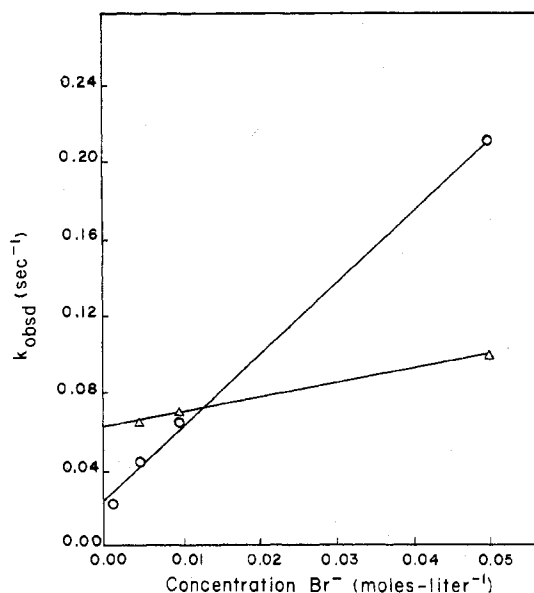

Figure 2. Dependence of k_{obsd} on the concentration of bromide ion: ○, reaction of [Au(Et$_2$dien-H)Cl]$^+$; △, reaction of [Au(Me$_4$dien-H)Cl]$^+$.

tion. Thus the rate constants k_{-2}, k_3, k_{-3}, k_4, and k_{-4} can be ignored as not contributing to the rate law governing the reaction. Therefore the steady-state concentration of species I is expressed by

$$[I] = \frac{k_1[R]}{k_{-1} + k_2[Br^-]} \quad (6)$$

Assuming that $k_{-1} \gg k_2[Br^-]$, the value of k_{Br} in Table IV may be related to the rate constant for this mechanism by

$$k_{Br} = k_1 k_2 / k_{-1} \quad (7)$$

Thus for [Au(Et$_2$dien-H)Cl]$^+$ the pseudo-first-order rate constant for bromide substitution is represented by

$$k_{obsd} = k_s + \frac{k_1 k_2}{k_{-1}}[Br^-] \quad (8)$$

A ring-opening equilibrium similar to that proposed in reaction 5 has been observed in amminediethylenetriamine-palladium(II) salts[5] and a similar mechanism has been suggested for the reaction of [Au(Et$_4$dien-H)Cl]$^+$ with N$_3^-$.[9]

Rationalization of the anomalously fast reaction rate for the bromide path in [Au(Et$_2$dien-H)Cl]$^+$ by eq 5 implies that the thermodynamic stability of the bond between the gold ion and the terminal tertiary nitrogen donor atom of Et$_2$dien-H is appreciably lower than the stability of the corresponding bonds in [Au(Me$_2$dien-H)Cl]$^+$ and [Au(Me$_4$dien-H)Cl]$^+$. Allison and Angelici found that ethyl substitution on the terminal nitrogens of diethylenetriamine decreases the formation constant of diethylenetriamine complexes of copper(II) to a greater extent than methyl substitution on these nitrogens.[14] Turan and Rorabacher have also reported such a difference in the stability of *N,N*-diethyl- *vs.* *N,N*-dimethylethylenediamines with Ni(II).[15] In a study of the formation and dissociation rates for the reaction of aquonickel(II) ion with *N,N*-diethyl-, *N,N'*-diethyl-, *N,N,N',N'*-tetramethyl-, and *N,N,N',N'*-tetraethylethylenediamine these authors found that the last ligand failed to coordinate. Furthermore, the *N,N*-diethylethylenediamine behaved as a mono-

(14) J. W. Allison and R. S. Angelici, *Inorg. Chem.*, **10**, 2233 (1971).

(15) T. S. Turan and D. B. Rorabacher, *Inorg. Chem.*, **11**, 288 (1972).

dentate ligand whereas the remaining two ligands behaved as bidentates. They concluded that increasing N-alkyl substitution leads to decreasing stability constants for second bond formation and attributed this trend to metal–ligand steric effects.

In the present study the larger charge on the Au(III) relative to Cu(II) and Ni(II) tends to oppose these metal–ligand steric effects and apparently is sufficient to enable the Et_2dien-H to behave as a tridentate ligand. However, the inherent weakness of the bond between the metal and the terminal tertiary nitrogen of the Et_2dien-H ligand favors the formation of species I in eq 5. This bidentate species is much more open to bromide ion attack and can easily pass through the distorted tetrahedral intermediate[16] depicted in eq 5 to form the product.

Registry No. [Au(Me₂dien-H)Cl]PF₆, 40354-46-9;

[Au(Me₂dien-H)Br]⁺, 40272-97-7; [Au(Me₂dien-H)OH]⁺, 40477-30-3; [Au(Me₂dien)Cl]²⁺, 40272-98-8; [Au(Et₂dien-H)Cl]PF₆, 40272-99-9; [Au(Et₂dien-H)Br]⁺, 40273-00-5; [Au(Et₂dien-H)OH]⁺, 40273-01-6; [Au(Et₂dien)Cl]²⁺, 40273-02-7; [Au(Me₄dien-H)Cl]PF₆, 40273-03-8; [Au(Me₄dien-H)Br]⁺, 40273-04-9; [Au(Me₄dien-H)OH]⁺, 40273-05-0; [Au(Me₄dien)Cl]²⁺, 40354-47-0; Br₂, 7726-95-6.

(16) The dihalogenated species is shown as a distorted tetrahedron with the "loose end" lying in the same plane as the Au–N bonds. Such a symmetrical intermediate is necessary to avoid violation of microscopic reversibility.

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Nuclear Magnetic Resonance Studies of the Solution Chemistry of Metal Complexes. VIII.[1] Ligand-Exchange Kinetics of the 1,3-Propylenediaminetetraacetic Acid and Ethylenediamine-N,N'-diacetic-N,N'-dipropionic Acid Complexes of Cadmium, Zinc, and Lead

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The kinetics of the ligand-exchange reactions of the 1,3-propylenediaminetetraacetic acid (1,3-PDTA) and ethylenediamine-N,N'-diacetic-N,N'-dipropionic acid (EDDDA) complexes of cadmium, zinc, and lead have been measured by nmr line-broadening methods. Rate constants were obtained for the proton-assisted dissociation of each of the complexes and for the displacement of complexed ligand by free ligand for several of the complexes. The rates of first-order dissociation of all of the complexes are too slow to measure by nmr line-broadening methods. Rate constants for the reaction of cadmium and zinc with monoprotonated 1,3-PDTA are approximately equal to those of the analogous reactions with monoprotonated ethylenediaminetetraacetic acid, while the rate constants for reaction of cadmium, zinc, and lead with monoprotonated EDDDA are from 2.5 to 10 times slower than the rate constants for reaction with monoprotonated 1,3-PDTA. Mechanisms are proposed for the complexation reactions of the monoprotonated ligands.

Introduction

The rates of complexation of divalent Cd,[2] Zn,[3] Co,[4] Cu,[5] and Ni[6] by the monoprotonated form of EDTA[7]

$$M^{2+} + HEDTA^{3-} \rightarrow M(EDTA)^{2-} + H^+ \qquad (1)$$
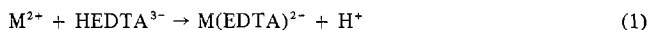
are all approximately equal to those predicted by the mechanism[8] in which dissociation of water from the aquated metal ions is rate determining.[9] However, the rates of complexation of Ca[10] and Sr[11] by the tetraanion of EDTA

$$M^{2+} + EDTA^{4-} \rightarrow M(EDTA)^{2-} \qquad (2)$$

are factors of $\leq 2.5 \times 10^2$ and 1.6×10^3 greater than their rates of complexation by HEDTA³⁻. Similarly, the rates of complexation of Ni[12] and Cd[13,14] by the trianion of NTA are 7×10^4 times greater than their rates of complexation by HNTA²⁻, while the rates of reaction of Zn[13] and Pb[15] with monoprotonated NTA (eq 3) are 3–4 orders of magnitude

$$M^{2+} + NTA^{3-} \rightarrow M(NTA)^- \qquad (3)$$

less than the approximate values predicted by the mechanism in which dissociation of water is rate determining.[16] Mechanisms proposed to account for these decreased rates either

(1) Part VII: S. Libich and D. L. Rabenstein, *Anal. Chem.*, 45, 118 (1973).

(2) N. Tanaka, R. Tamanushi, and M. Kodama, *Z. Phys. Chem. (Frankfurt am Main)*, 14, 141 (1958); J. L. Sudmeier and C. N. Reilley, *Inorg. Chem.*, 5, 1047 (1966).

(3) G. H. Reed and R. J. Kula, *Inorg. Chem.*, 10, 2050 (1971).

(4) N. Tanaka, *Bull. Chem. Soc. Jap.*, 36, 67 (1963).

(5) N. Tanaka, H. Osawa, and M. Kamada, *Bull. Chem. Soc. Jap.*, 36, 530 (1963).

(6) D. W. Margerum and B. A. Zabin, *J. Phys. Chem.*, 66, 2214 (1962).

(7) Abbreviations used: EDTA, ethylenediaminetetraacetic acid; 1,3-PDTA or L, 1,3-propylenediaminetetraacetic acid; EDDDA or L, ethylenediamine-N,N'-diacetic-N,N'-dipropionic acid; NTA, nitrilotriacetic acid.

(8) M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, No. 49, 61 (1965); R. G. Wilkins, *Accounts Chem. Res.*, 3, 408 (1970).

(9) D. W. Margerum, P. J. Menardi, and D. L. Janes, *Inorg. Chem.*, 6, 283 (1967).

(10) R. J. Kula and G. H. Reed, *Anal. Chem.*, 38, 697 (1966).

(11) R. J. Kula and D. L. Rabenstein, *J. Amer. Chem. Soc.*, 89, 552 (1967).

(12) T. J. Bydalek and M. L. Blomster, *Inorg. Chem.*, 3, 667 (1964).

(13) D. L. Rabenstein and R. J. Kula, *J. Amer. Chem. Soc.*, 91, 2492 (1969).

(14) N. Tanaka, E. Ebata, T. Takahari, and T. Kumagai, *Bull. Chem. Soc. Jap.*, 35, 1836 (1962).

(15) D. L. Rabenstein, *J. Amer. Chem. Soc.*, 93, 2869 (1971).

(16) The water loss rate constant for aquated Pb(II) has been reported to be approximately the same as that of Hg(II): M. Eigen, *Pure Appl. Chem.*, 6, 97 (1963).