reactant carbonyl. The peak height to infinite time could be neglected from the calculations.

The two reactions that were run at specified starting acid concentrations had aqueous fluoroboric acid added to the stock solution at the beginning of the experiment.

(c) **Reaction of Fe(π-C$_5$H$_5$)(CO)$_2$(COOCH$_3$) with Water.**—In an evacuated Pyrex tube, freshly sublimed[6] Fe(π-C$_5$H$_5$)(CO)$_2$(COOCH$_3$) (0.25 g, 1.1 mmol) was shaken at 45° for 20 min in degassed water (1 ml) containing KCl (1.0 g). Effervescence was observed during the reaction and a deep red liquid, immiscible in water, and a black solid were obtained. The volatile products were distilled under vacuum through traps at −25, −96, and −196° traps. The trap at −196° contained carbon dioxide (0.036 g, 0.8 mmol) identified by infrared spectroscopy. Two less volatile products were isolated; one was characterized as methanol by infrared and nmr spectroscopy, and the other was tentatively identified by infrared spectroscopy as methyl formate.[9] The trap at −25° contained water and a red liquid identified as Fe(π-C$_5$H$_5$)(CO)$_2$H (0.09 g, 0.52 mmol) by infrared and ^{1}H nmr spectroscopy[10] (hydride chemical shift, τ 21 in CHCl$_3$). The nonvolatile products were extracted with chloroform and the chloroform extract contained the dimer [Fe(π-C$_5$H$_5$)(CO)$_2$]$_2$ (0.08 g, 0.44 mmol) identified by infrared spectroscopy. The residue, a white solid, was assumed to be KCl. On exposure of the hydrido compound to the atmosphere, reaction to the black dimer was complete within 1 min.

Identical results were obtained when the above reaction was repeated without the salt.

(d) **Reaction of Mn(CO)$_5$(COOC$_2$H$_5$) with Water.**—In a Pyrex tube, freshly sublimed Mn(CO)$_5$(COOC$_2$H$_5$)[8] (0.28 g, 1.0 mmol) was shaken at 75° for 12 hr with KCl (1.0 g) and 4 ml of water. A viscous oil, immiscible in water, was left after reaction. The volatile products were distilled through traps at −25, −96, and −196°. The trap at −196° contained carbon dioxide (0.039 g, 0.9 mmol) identified by infrared spectroscopy.

The other traps contained water and ethanol, characterized by infrared and proton nmr spectroscopy, and a yellow liquid characterized by infrared[11] and nmr spectroscopy[10] (hydride chemical shift, τ 18 in CHCl$_3$) as Mn(CO)$_5$H (0.12 g, 0.6 mmol). The nonvolatile products contained a yellow solid, identified by infrared spectroscopy as the dimeric compound Mn$_2$(CO)$_{10}$ (0.06 g, 0.3 mmol), and a white water-soluble solid assumed to be KCl. Infrared spectrum of HMn(CO)$_5$ as gas: ν(CO) 2035 (vs), 2030 (vs), 2025 (vs), 2015 (vs), 2130 (w), 2125 (w), 2120 (w), 2100 (w), 2050 (w) and 2045 (w) cm^{-1}.

The above reaction was repeated without potassium chloride and, although trace amounts of ethyl formate were isolated in the volatile products, the reaction was basically unchanged.

(9) H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945).

(10) A. Davison, J. A. McCleverty, and G. Wilkinson, *ibid.*, 1133 (1963).

(11) F. A. Cotton, J. L. Down, and G. Wilkinson, *ibid.*, 833 (1959).
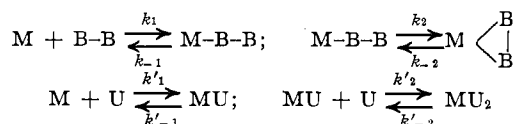
The Kinetic Chelate Effect. Chelation of Ethylenediamine on Platinum(II)

BY MARK J. CARTER AND JAMES K. BEATTIE

A kinetic explanation is offered for the chelate effect, based on observation of the rates of ethylenediamine ring closure in square-planar *trans*-dichlorobis(ethylenediamine)platinum(II). Stopped-flow spectrophotometry in basic solution gave rate constants at 25° in 1 M LiClO$_4$ of 10.4 ± 0.6 and 0.73 ± 0.06 sec^{-1} for the first and second ring closures, respectively. By pH-stat titrimetry in acidic solution the acid dissociation constants of monodentate ethylenediamine were determined. These results are compared with analogous substitutions by ammonia to determine the kinetic origin of the chelate effect. Comparison with other observations on nickel(II)–ethylenediamine complexes provides an interesting distinction between the kinetic chelate effects in octahedral and square-planar complexes.

Introduction

The increased thermodynamic stability of complexes of multidentate ligands relative to those of unidentate ligands is well known and has been extensively investigated.[1] This chelate effect must be reflected in the kinetics of complex formation as well as in stabilities. A further examination of the kinetic chelate effect is the subject of this paper. Consider the reactions

$$M + B-B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M-B-B; \quad M-B-B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} M \overset{B}{\underset{B}{\diagdown}}$$

$$M + U \underset{k'_{-1}}{\overset{k'_1}{\rightleftarrows}} MU; \quad MU + U \underset{k'_{-2}}{\overset{k'_2}{\rightleftarrows}} MU_2$$

$$K_B = \frac{\left[M\overset{B}{\underset{B}{\diagdown}}\right]}{[M][B-B]} = \frac{k_1 k_2}{k_{-1} k_{-2}}$$

$$K_U = \frac{[MU_2]}{[M][U]^2} = \frac{k'_1 k'_2}{k'_{-1} k'_{-2}}$$

in which B–B is a bidentate ligand and U is unidentate. The additional stability of the chelate complex means $K_B > K_U$ which requires

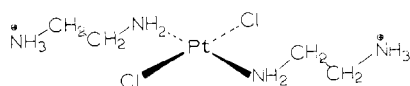$$\frac{k_1 k_2}{k_{-1} k_{-2}} > \frac{k'_1 k'_2}{k'_{-1} k'_{-2}}$$

It is sometimes assumed that the first steps of these reactions are not sensitive to differences between otherwise similar unidentate and bidentate ligands, except

(1) For a recent review see A. E. Martell, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1967, p 272.

for a statistical factor of 2.[2] In this interpretation, the chelate effect requires $(k_2/k_{-2}) > (k'_2/k'_{-2})$.

Measurements of rate constants k_2 are uncommon. Since k_2 is usually much larger than $k_1[B-B]$ or k_{-1}, studies of the overall rates of formation of chelate complexes generally yield only k_1, whereas studies of dissociation reactions give the ratio $k_{-1}k_{-2}/k_2$. There have been several studies of the chelate ring closure step in octahedral complexes for which the activation process is primarily dissociative.[3] In square-planar substitution reactions, in contrast, the activation process is primarily associative and the chelate effect on the rate of substitution may be more dramatic. Some kinetic evidence for the effects of chelation on substitution on platinum(II) has been reported but in the systems studied direct comparisons with substitution by unidentate ligands on analogous complexes were not possible.[4]

We have prepared the *trans*-dichlorobis(ethylenediamine monohydrochloride)platinum(II) ion and have studied the rate of ring closure in both acidic and basic solution. The study in basic solution using rapid-

mixing stopped-flow spectrophotometry permitted direct measurement of rate constants k_2 for each ring closure. The results can be compared directly with the rates of substitution by unidentate ammonia in the analogous chloroammine complexes of platinum(II). Comparison with the mechanism of chelation on octahedral complexes indicates an interesting difference in the kinetic chelate effect for square-planar and octahedral complexes.

Experimental Section

Materials—Bis(ethylenediamine)platinum(II) chloride was prepared according to Basolo, Bailar, and Tarr.[5] *Anal.* Calcd for [Pt(en)₂]Cl₂: Pt, 50.5; C, 12.4; H, 4.2; Cl, 18.2. Found: Pt, 50.3; C, 12.5; H, 4.1; Cl, 18.4.

trans-Dichlorobis(ethylenediamine monohydrochloride)platinum(II) was prepared essentially as described by Drew.[6] 80 ml of concentrated HCl was added to 4.85 g of [Pt(en)₂]Cl₂ dissolved in a minimum amount of water. The solution was heated on a steam bath for 6–7 hr or until several milliliters of liquid was left with the solid mixture. The mixture was allowed to cool and stand at room temperature for 1 hr. After cooling in ice, the solid was removed by filtration and washed with dilute HCl followed by ether. This product is a mixture from which the desired compound was obtained by placing several grams of the mixture in a 2-ml medium sintered glass funnel and washing with several small portions of approximately 0.1 *M* HCl. Insoluble bright yellow Pt(en)Cl₂ was retained on the filter. Concentrated HCl (5 ml) was immediately added dropwise to the filtrate and

the pale yellow solid which precipitated was immediately collected and washed with dilute HCl followed by ether. White [Pt(en)₂]Cl₂ can be recovered from the filtrate on cooling in ice. The desired product was air dried on a watch glass. Difficulty was experienced with some samples which developed a pink tint on drying, in which cases the material was recrystallized. *Anal.* Calcd for [Pt(enH)₂Cl₂]Cl₂: Pt, 42.5; Cl, 30.9; C, 10.5; H, 4.0. Found: Pt, 42.3; Cl, 31.0; C, 10.9; H, 4.0. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry and Chemical Engineering, University of Illinois.

Lithium perchlorate solutions were prepared either from recrystallized G. F. Smith anhydrous LiClO₄ or from LiClO₄ prepared from Fisher Li₂CO₃ and G. F. Smith HClO₄ and recrystallized once. Sodium hydroxide solutions were prepared from Anachemia Chemical Acculute standard NaOH.

Kinetics Experiments.—Rate data in acidic solutions were obtained using a Radiometer pH-stat recording titrator consisting of a Type SBR2c titrigraph, PHM26c pH meter, TTT 11 titrator, and SBU1a syringe buret. The KCl in the calomel electrode was replaced by 4 *M* NaCl to prevent precipitation of KClO₄. This resulted in an increase in indicated pH values of 0.40, constant in the pH range 3.0–5.0. All reported pH values have been corrected to refer to a standard calomel reference electrode.

The stopped-flow experiments in basic solutions were performed using the apparatus described previously but with the Beckman DU monochromator replaced with a 0.25-m Jarrell-Ash grating monochromator, with appropriate changes in the source optics.[7]

Results

The "open-ring" complex ion *trans*-Pt(enH)₂Cl₂²⁺ is stable in acidic solution of pH 0, but at lower acidities, pH 3–5, a two-step reaction occurs with release of two hydrogen ions for each complex ion, indicating ring closure. The rate of the reaction is pH dependent, but by using the pH-stat titrator it is possible to maintain a constant pH by incremental addition of base to neutralize the acid produced in the reaction. With this technique one can measure the rate of the reaction, which is precisely the rate at which base must be added to maintain a constant pH, without the use of buffers.

The experiments were performed in an ionic medium of 1.0 *M* LiClO₄ using $(3.2-7.3) \times 10^{-3}$ *M* initial concentration of complex and 0.01–0.06 *M* NaOH titrant. The consumption of base resulting from dilution at a constant pH was insignificant compared with that required to neutralize the acid produced in the reaction. The rates of both steps of the reaction were observed to be inversely dependent on hydrogen ion concentration with the first step occurring at a significantly faster rate than the second. This permitted the first step to be observed in a convenient time range at pH 3.1–3.6. Similarly, the second step could be observed conveniently in the pH range 4.0–4.7 after the first step was substantially complete. The Guggenheim method[8] was used to obtain estimates of the first-order rate constants for both the first and second steps in these pH ranges, using the first third of the overall reaction to obtain $k_{1,obsd}$ and the last third to obtain $k_{2,obsd}$. The Guggenheim method is not strictly appropriate to the treatment of successive first-order reactions

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, New York, N.Y., 1967, p 223.

(3) (a) A. Kowalak, K. Kustin, R. F. Pasternack, and S. Petrucci, *J. Am. Chem. Soc.*, **89**, 3126 (1967); (b) W. B. Makinen, A. F. Pearlmutter, and J. E. Stuehr, *ibid.*, **91**, 4083 (1969); (c) A. G. Sykes and R. N. F. Thorneley, *J. Chem. Soc.*, A, 655 (1969); (d) J. P. Jones and D. W. Margerum, *J. Am. Chem. Soc.*, **92**, 470 (1970).

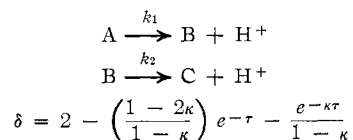(4) S. P. Tanner, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **6**, 1089 (1967).

(5) F. Basolo, J. C. Bailar, Jr., and B. R. Tarr, *J. Am. Chem. Soc.*, **72**, 2433 (1950).

(6) H. D. K. Drew, *J. Chem. Soc.*, 2328 (1932).

(7) S. A. Frennesson, J. K. Beattie, and G. P. Haight, Jr., *J. Am. Chem. Soc.*, **90**, 6018 (1968).

(8) (a) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926); (b) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, New York, N. Y., 1961.

unless the rate constants differ substantially. Consequently, an iterative least-squares program was written for an IBM 1800 computer to obtain the best values of $k_{1,obsd}$ and $k_{2,obsd}$ necessary to fit the complete concentration–time curve. The function δ represents the total amount of hydrogen ion released as a function of time for the following reaction sequence if only A is present initially.[8b]

$$A \xrightarrow{k_1} B + H^+$$

$$B \xrightarrow{k_2} C + H^+$$

$$\delta = 2 - \left(\frac{1 - 2\kappa}{1 - \kappa}\right) e^{-\tau} - \frac{e^{-\kappa\tau}}{1 - \kappa}$$

where $\kappa = k_2/k_1$ and $\tau = k_1 t$. Starting with estimates of k_1 and k_2 obtained from the Guggenheim plots, the program iterated k_1 and k_2 to obtain the best fit of the calculated δ with the observed curve, which was generally within a standard deviation of 0.5%. Four experiments were performed in the pH range 3.40–3.90 chosen to provide the maximum overlap of the two steps in a convenient time range. The values obtained are plotted in Figure 1 as a function of inverse hydrogen ion concentration. From these plots the slope for the first step is $(1.22 \pm 0.05) \times 10^{-7} M$ sec^{-1}. For the second step the slope is $(7.67 \pm 0.20) \times 10^{-9} M$ sec^{-1} and the intercept is $(1.4 \pm 0.2) \times 10^{-5}$ sec^{-1}.

The rates of the reaction in basic solution were obtained spectrophotometrically by rapid mixing of a solution of *trans*-Pt(enH)$_2$Cl$_2{}^{2+}$ dissolved in 1.0 M LiClO$_4$ containing 0.01 M HClO$_4$ with a second solution of 1.0 M LiClO$_4$ containing sufficient NaOH to bring the pH of the mixed solution above 11. The appropriate spectra are shown in Figure 2. The spectrum of the "open-ring" starting material was obtained in acidic solution. It is assumed that protonation of the noncoordinated amine will not alter the spectrum significantly from that which would be observed for the nonprotonated "open-ring" complex Pt(en)$_2$Cl$_2$ in basic solution. The spectrum of the product Pt(en)$_2{}^{2+}$ could be obtained directly. An approximate spectrum of the intermediate was obtained by allowing a reaction on the pH-stat to proceed about halfway to completion and then quenching the reaction by adding acid to reduce the pH to 0–1. It is apparent that in the region 385–400 nm the first ring-closing reaction can be observed directly without interference from the second step. Observation in the region 250–290 nm should reveal an increase in absorbance due to the first step of the reaction followed by a decrease associated with the second step. Figure 3 reproduces an oscilloscope trace of the absorbance changes at 250 nm which demonstrates these changes. The first-order rate constants of the two reactions were obtained from conventional plots of log $(D - D_\infty)$ against time. The value of $k_1 = 10.4 \pm 0.6$ sec^{-1} was independent of wavelength from 385 to 400 nm and that of $k_2 = 0.73 \pm 0.06$ sec^{-1} from 260 to 295 nm.

Discussion

The excellent fit of the data obtained in acidic solution to that calculated for consecutive first-order reactions
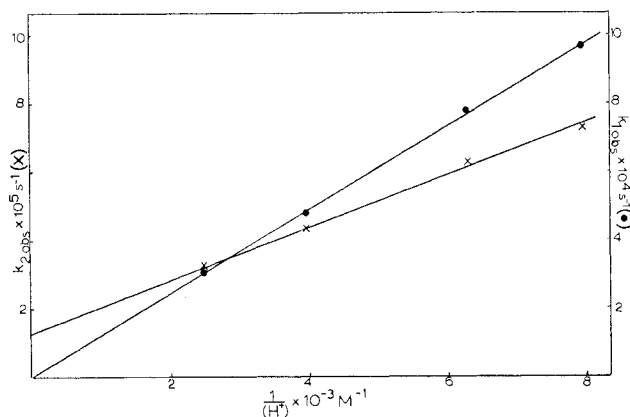

Figure 1.—Hydrogen ion concentration dependence of $k_{1,obsd}$ and $k_{2,obsd}$ obtained by a least-squares fit of the observed titration–time curve.
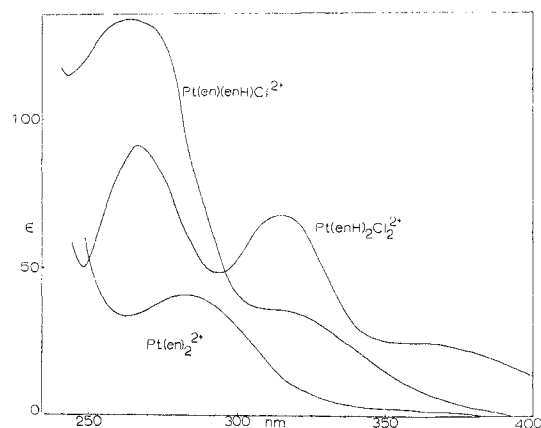

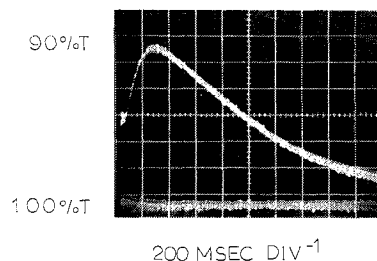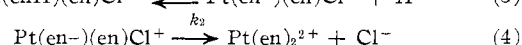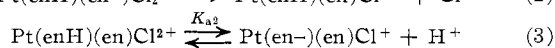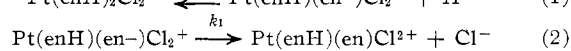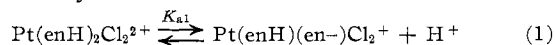Figure 2.—Solution absorption spectra of starting material, intermediate, and product.

Figure 3.—Oscillographic trace of absorbance changes at 250 nm.

strongly indicates that the observed reactions are indeed the chelate ring closings of two unidentate ethylenediamine ligands. The observed pH dependence is readily explained by this mechanism after recognizing that the free amine group must be unprotonated in order to bond to the platinum. The ring-closure step (eq 2) is therefore preceded by a rapid acid–base equilibrium (eq 1). For the acid-dependent terms of the first and second steps, reactions 1–4 are suggested, where enH denotes unidentate protonated ethylenediamine ligand, en– a unidentate unprotonated ligand, and en the usual bidentate ethylenediamine. The formal rate law for

$$\text{Pt(enH)}_2\text{Cl}_2{}^{2+} \underset{\phantom{K_{a1}}}{\overset{K_{a1}}{\rightleftharpoons}} \text{Pt(enH)(en-)Cl}_2{}^+ + \text{H}^+ \qquad (1)$$

$$\text{Pt(enH)(en-)Cl}_2{}^+ \xrightarrow{k_1} \text{Pt(enH)(en)Cl}^{2+} + \text{Cl}^- \qquad (2)$$

$$\text{Pt(enH)(en)Cl}^{2+} \underset{\phantom{K_{a2}}}{\overset{K_{a2}}{\rightleftharpoons}} \text{Pt(en-)(en)Cl}^+ + \text{H}^+ \qquad (3)$$

$$\text{Pt(en-)(en)Cl}^+ \xrightarrow{k_2} \text{Pt(en)}_2{}^{2+} + \text{Cl}^- \qquad (4)$$

the appearance of the $Pt(en)(enH)Cl^{2+}$ intermediate by reactions 1 and 2 is

$$\frac{d[Pt(en)(enH)Cl^{2+}]}{dt} = \frac{k_1 K_{a1}}{K_{a1} + [H^+]}[Pt(en)(enH)Cl^{2+}] \quad (5)$$

which reduces in the case $K_{a1} \ll [H^+]$ to a first-order rate law with
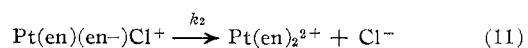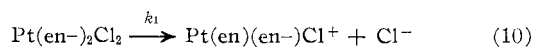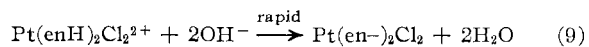
$$k_{obsd} = \frac{k_1 K_{a1}}{[H^+]} \quad (6)$$

Results described below indicate $K_{a1} \approx 10^{-8} M$ which justifies the assumption that $K_{a1} \ll [H^+]$ for solutions of pH 3–5. Consequently the slopes of the plots in Figure 1 may be interpreted as $k_1 K_{a1}$ and $k_2 K_{a2}$, respectively.

The nonzero intercept observed in Figure 2 for the second step indicates that in addition to reactions 3 and 4 there must be an acid-independent mechanism, presumably the usual solvent pathway frequently observed for square-planar substitution reactions

$$Pt(en)(enH)Cl^{2+} \xrightarrow{k_0} Pt(en)(enH)H_2O^{3+} + Cl^- \quad (7)$$

$$Pt(en)(enH)(H_2O)^{3+} \xrightarrow{rapid} Pt(en)_2^{2+} + H^+ + H_2O \quad (8)$$
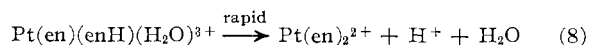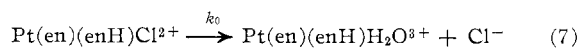
The intercept is then interpreted as k_0. Within experimental error there is no evidence for a solvent path in the first step.

Mixing an acidic solution of $Pt(enH)_2Cl_2^{2+}$ with base results in rapid deprotonation (eq 9) of the uncoordinated amine groups. These then close by reactions 10 and 11. The spectral changes observed are exactly

$$Pt(enH)_2Cl_2^{2+} + 2OH^- \xrightarrow{rapid} Pt(en-)_2Cl_2 + 2H_2O \quad (9)$$

$$Pt(en-)_2Cl_2 \xrightarrow{k_1} Pt(en)(en-)Cl^+ + Cl^- \quad (10)$$

$$Pt(en)(en-)Cl^+ \xrightarrow{k_2} Pt(en)_2^{2+} + Cl^- \quad (11)$$

those expected for this sequence of reactions. It is fortunate that there is a region of the spectrum (380–400 nm) in which (10) can be observed without interference from (11), which avoids some of the difficulties associated with the analysis of consecutive first-order reactions.

K_{a1} and K_{a2} can be evaluated if the assumption is made that k_1 and k_2 obtained spectrophotometrically from reactions 10 and 11 are equivalent to k_1 and k_2 of reactions 2 and 4, even though the reacting species in (2) differs from that in (10) by an additional proton. The values obtained are $(1.2 \pm 0.1) \times 10^{-8} M$ and $(1.1 \pm 0.2) \times 10^{-8} M$ for K_{a1} and K_{a2}, respectively. These can be compared with the first and second ionization constants of 3.4×10^{-8} and $6.8 \times 10^{-11} M$ for enH_2^{2+}.[9] Thus coordinated ethylenediamine is a slightly weaker acid than diprotonated ethylenediamine, but considerably stronger than monoprotonated ethylenediamine. The various constants evaluated from the kinetic data are assembled in Table I.

Comparisons can be made between these results and substitution reactions on related platinum(II) com-

(9) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," *Special Publication No. 17*, The Chemical Society, London, 1964, p 370.

TABLE I
PARAMETERS IN 1.0 M LiClO$_4$ AT 25°

$k_1 K_{a1}$	$(1.22 \pm 0.05) \times 10^{-7} M \, sec^{-1}$
k_1	$10.4 \pm 0.6 \, sec^{-1}$
K_{a1}	$(1.2 \pm 0.1) \times 10^{-8} M$
$k_2 K_{a2}$	$(7.67 \pm 0.20) \times 10^{-9} M \, sec^{-1}$
k_2	$0.73 \pm 0.06 \, sec^{-1}$
K_{a2}	$(1.1 \pm 0.1) \times 10^{-8} M$
k_{02}	$(1.4 \pm 0.2) \times 10^{-5} \, sec^{-1}$

plexes in which chelation is not involved in the rate-determining step. Some of the relevant data from the literature are assembled in Table II. Other investigations have indicated that substitutions by ammonia on chloroammine complexes of platinum(II) are not strongly dependent on ionic strength, so comparisons will be made freely without regard to the medium used in the experiments reported. Another useful feature observed by comparing reactions A and B (in Table II) is that the influence of coordinated ethylenediamine on the rate of substitution of the remaining chlorides by ammonia is very similar to that of *cis*-coordinated ammonia ligands, so that comparisons can be made directly between ammine and ethylenediamine complexes. The first striking feature of our results is that the ratio of rate constants for the first and second steps, $k_1/k_2 = 14 \pm 2$, is very similar to the ratio of rates of reactions C and D, $k_c/k_d = 11$. This ratio could be considered as a measure of the *trans* effect of chloride, *i.e.*, the relative ease of substitution of a chloride by an amine on a chloro–chloro axis *cis* to an amine–amine axis compared to substitution on a chloro–amine axis *cis* to an amine–amine axis. This *trans* effect of chloride relative to an amine is the same whether the substitution is a bimolecular process involving ammonia or a unimolecular chelate ring closing of ethylenediamine. This similarity strongly suggests that the chelate ring closing is very similar to that of a normal bimolecular square-planar substitution reaction.

Further support for this interpretation of the mechanism of chelate ring closing is obtained from observation of the solvent path for the second step with a rate constant of $1.4 \times 10^{-5} \, sec^{-1}$ which is similar to that of $2.6 \times 10^{-5} \, sec^{-1}$ observed for reaction J. A solvent path for the first step would also be expected with a rate constant of approximately $6 \times 10^{-5} \, sec^{-1}$ if the analogy with reaction I can be pressed, but due to the more rapid ring closure in the first step this path may be lost in the experimental error. Careful experiments at much higher acidities would be necessary to determine if this path is present.

The question remains as to why the chelation reactions are substantially faster than substitution by ammonia. The first ring closure is approximately 1800 times faster than the analogous reaction C in 1 M NH$_3$ and the second 1400 times faster than reaction D in 1 M NH$_3$. One reason for the faster rates is the greater nucleophilicity of ethylenediamine relative to ammonia. Comparisons of reaction E with reaction F and of reaction G with reaction H indicate that ethylenediamine is 5.4 and 3.4 times more reactive than ammonia

TABLE II

	Reaction	Conditions	k, M^{-1} sec^{-1}	Ref
A.	NH_3 + cis-$Pt(NH_3)_2Cl_2$ → $Pt(NH_3)_3Cl^+$ + Cl^-	35°, I = 0.3	4.8×10^{-4}	a
B.	NH_3 + $Pt(en)Cl_2$ → $Pt(NH_3)(en)Cl^+$ + Cl^-	35°, I = 0.1	5×10^{-4}	b
C.	NH_3 + $trans$-$Pt(NH_3)_2Cl_2$ → $Pt(NH_3)_3Cl^+$ + Cl^-	25°, I = 0.3	5.7×10^{-3}	a
D.	NH_3 + $Pt(NH_3)_3Cl^+$ → $Pt(NH_3)_4^{2+}$ + Cl^-	25°, I = 0.3	5.4×10^{-4}	a
E.	en + $PtCl_4^{2-}$ → $Pt(en)Cl_2$ + $2Cl^-$	25°	2×10^{-3}	c
F.	NH_3 + $PtCl_4^{2-}$ → $Pt(NH_3)Cl_3^-$ + Cl^-	25°, I = 0.3	3.7×10^{-4}	a
G.	en + $Pt(NH_3)Cl_3^-$ → $Pt(en)(NH_3)Cl^+$ + $2Cl^-$	25°	3.7×10^{-3}	c
H.	NH_3 + $Pt(NH_3)Cl_3^-$ → $Pt(NH_3)_2Cl_2$ + Cl^-	25°, I = 0.3	1.1×10^{-3}	a
I.	H_2O + $trans$-$Pt(NH_3)_2Cl_2$ → $Pt(NH_3)_2H_2OCl^+$ + Cl^-		9.8×10^{-5} e	d
J.	H_2O + $Pt(NH_3)_3Cl^+$ → $Pt(NH_3)_3H_2O^{2+}$ + Cl^-		2.6×10^{-5} e	d

a C. B. Colvin, R. G. Gunther, L. D. Hunter, J. A. McLean, M. A. Tucker, and D. S. Martin, Jr., *Inorg. Chim. Acta*, **2**, 487 (1968).
b U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965). c Yu. N. Kukushkin and V. B. Ukraintsev, *Russ. J. Inorg. Chem.*, **13**, 1485 (1968). d M. A. Tucker, C. B. Colvin, and D. S. Martin, Jr., *Inorg. Chem.*, **3**, 1373 (1964).
e In sec^{-1}.

on the respective complexes. Thus, after allowing for this effect and a statistical factor of 2, the chelate ring closing reactions are about 800 times faster than a normal bimolecular substitution, in which the concentration of the entering group is 1 M.

A significant factor in this rate enhancement is certainly the higher effective concentration of the entering group—a neighboring group effect or anchimeric assistance. The ring closure of unidentate ethylenediamine is a first-order, unimolecular reaction, whereas the substitution by ammonia is a second-order, bimolecular process. To make a proper comparison between the two rate constants one must convert the first-order rate constant (sec^{-1}) to a second-order rate constant (M^{-1} sec^{-1}) by assuming an effective concentration of the entering ethylenediamine group. This effective concentration is certainly greater than 1 M, resulting in a faster rate of ring closure than of substitution. An effective concentration of 800 M is far too high, however, for this corresponds to a molecular concentration of 0.5 molecule Å^{-3}.

Cotton and Harris have performed a statistical analysis of the distribution of the free end of a chelate ring and found that the maximum probability occurred at about 4–5 Å.[10] Assuming that the free end filled a hemisphere of minimum radius 3 Å, the effective concentration would be about 0.02 molecule Å^{-3}, or 30 M. One must conclude that the higher effective concentration is not the only reason for the faster rate of ring closure and that other, presumably more specific, influences are important. These conclusions are consistent with the observations that both entropy and enthalpy effects influence the equilibrium chelate effect.

Equilibrium constants are not available for the relatively inert and stable platinum(II)–amine complexes. They have recently been reported, however, for the analogous palladium(II) complexes.[11] The formation constant of $Pd(en)(H_2O)_2^{2+}$ could not be measured but for the reaction

$$Pd(en)(H_2O)_2^{2+} + en \underset{}{\overset{K_2}{\rightleftarrows}} Pd(en)_2^{2+} + 2H_2O \qquad (12)$$
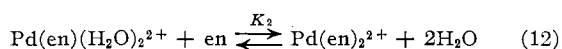
$\log K_2$ = 18.4. In contrast, for formation of the tri- and tetraammine–palladium(II) complexes, $\log K_3$ +

$\log K_4$ = 14.3. In other words the chelate effect is on the order of 10^4. Making the gross assumption that the Pt(II) complexes are similar, we observe that the kinetic effect of rapid ring closure accounts for a factor of 10^3. Assuming that the ratio k_1/k_{-1} is the same for unidentate and bidentate ligands, the discrepancy implies that k_{-2} is perhaps an order of magnitude smaller for the chelate complex than for the unidentate complex. Other authors have previously observed that ring opening in a chelate complex involves a steric restriction because the ring is required to open in one specific direction, that is, in order to form the unidentate complex.[12] It is estimated that the energy barrier to ring opening could result in a decrease in rate by about a factor of 40,[13] the correct order of magnitude to account for the chelate effect if the analogy made here between Pd(II) and Pt(II) complexes is valid. The equilibrium chelate effect in square-planar complexes is thus a consequence of kinetic effects in both the ring-closing and ring-opening steps, k_2 and k_{-2}, in addition to a small effect on k_1.

It is instructive to compare these observations with those made on an octahedral complex, $Ni(H_2O)_4(en).^{2+}$ Numerous studies have established that most substitution reactions on octahedral complexes proceed by a dissociative mechanism with rates dependent primarily on the rate of dissociation of water from the metal ion. Although it is erroneous to deduce effects on equilibrium constants from consideration of the mechanism of a reaction in the forward direction alone, the principle of microscopic reversibility requires that the equilibrium constant reflect the ratio of rate constants for the forward and reverse reactions. If it is argued that in the octahedral system both the forward and the reverse reaction rates are determined by the rates of dissociation, in the forward reaction that of water and in the reverse reaction that of the amine ligand, and if it is further assumed that the rates of dissociation of ethylenediamine and ammonia are similar, except for the steric factor mentioned above resulting in a smaller k_{-2} for ethylenediamine, then the equilibrium chelate effect is expected to be small for $Ni(en)^{2+}$. In fact the available

(10) F. A. Cotton and F. E. Harris, *J. Phys. Chem.*, **60**, 1451 (1956).
(11) L. Rasmussen and C. K. Jørgensen, *Acta Chem. Scand.*, **22**, 2313 (1968).
(12) A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 3700 (1959).
(13) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).

stability constants[9] indicate that the chelate effect is substantially smaller for octahedral nickel(II) than for square-planar palladium(II), on the order of 100–200 for $Ni(en)^{2+}$ compared with $Ni(NH_3)_2^{2+}$, in contrast to the value of 10^4 indicated above for palladium(II). Thus the general distinction between dissociative modes of reaction for octahedral complexes and associative modes for square-planar complexes nicely parallels the difference in the relative magnitudes of the equilibrium chelate effect.

A kinetic explanation for the chelate effect in octahedral complexes thus depends on the smaller rate of ring opening of ethylenediamine relative to dissociation of ammonia, resulting in $(k_2/k_{-2}) > (k'_2/k'_{-2})$, and on the possible influence of internal conjugate base formation by ethylenediamine, suggested by Rorabacher.[14] Substitution of $Ni(H_2O)_6^{2+}$ by ethylenediamine is some 50 times faster than substitution by ammonia, an observation inconsistent with the simple model of a dissociative mechanism. Rorabacher proposed that the second amine group of the diamine forms a hydrogen bond with a coordinated water, forming an incipient conjugate base on the nickel(II) ion. This results in more rapid loss of water from the metal ion and an enhanced rate of substitution by the first amine group of the diamine

(14) D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

The larger value of k_1 for ethylenediamine relative to ammonia does not account for the chelate effect, however, for if the transition-state energy for the process represented by k_1 is lowered by internal conjugate base formation, then according to the principle of microscopic reversibility the transition-state energy for the reverse process k_{-1} is lowered similarly and the ratio of the rates k_1/k_{-1} remains constant.

An explanation of the chelate effect is provided by a simple extension of the internal conjugate base mechanism. Although there is no direct experimental evidence available, it seems reasonable that in the half-bonded intermediate $Ni(H_2O)_5(en-)^{2+}$ the free end of the amine will remain hydrogen bonded as in the transition state and will be consequently more stable. The chelate effect may thus reflect a larger value of $K_1 = k_1/k_{-1}$ for ethylenediamine relative to ammonia. Thus, in contrast to substitution on a square-planar complex in which the larger value of k_2 is responsible for the kinetic chelate effect, in the octahedral system the origin of the kinetic chelate effect is in k_1/k_{-1}, as well as in a smaller value of k_{-2} common to both systems. The chelate effect, which is observed for both square-planar and octahedral complexes, must be explained kinetically by distinctly different mechanisms, a consequence of the distinctly different modes of reactivity of the two classes of complexes.

Ternary Complexes in Solution. VIII. Complex Formation between the Copper(II)–2,2'-Bipyridyl 1:1 Complex and Ligands Containing Oxygen and/or Nitrogen as Donor Atoms[1,2]

By ROLF GRIESSER and HELMUT SIGEL[3]

The stability constants of the ternary Cu^{2+} complexes containing 2,2'-bipyridyl and as a second ligand ethylenediamine, glycine anion, malonic acid dianion, or pyrocatechol dianion were determined by potentiometric titration. For the equilibrium $CuA_2 + CuB_2 \rightleftharpoons 2CuAB$, the corresponding constants are log X = 1.10, 3.05, 5.49, and 6.15 (I = 0.1; temperature 25°). All four ternary complexes are more stable than one would expect for purely statistical reasons (log X = 0.6). Furthermore, the stability constants show that the Cu^{2+}–2,2'-bipy 1:1 complex has discriminating qualities toward the second ligand to be coordinated; it rather prefers to form ternary complexes with those ligands that contain O as donor atoms. In addition, the formation constants for the reactions between the Cu^{2+}–2,2'-bipy 1:1 complex and the dianions of malonic acid or pyrocatechol are greater than those for the corresponding reactions with the free (hydrated) Cu^{2+} ion. To get a broader basis for the evaluation of the reasons for the high stability of these ternary complexes, results taken from the literature were included in the Discussion. The conclusions drawn from a total of 20 examples of ternary Cu^{2+} complexes are that the most important driving forces for the formation of ternary complexes are electronic effects (π system of the ligands), besides coulombic effects (neutralization of charge in ternary complexes), and lower steric hindrance compared with the corresponding binary bis complexes.

In several papers it has been stated that ligands containing O as donor atoms form stabler complexes

with the Cu^{2+}–2,2'-bipy 1:1 complex (eq 1) than with the free (hydrated) Cu^{2+} ion (eq 2). Hence, according to eq 3 positive Δ log K values were ob-

$$Cu(bipy) + L \rightleftharpoons Cu(bipy)L$$

$$K^{Cu(bipy)}_{Cu(bipy)L} = \frac{[Cu(bipy)L]}{[Cu(bipy)][L]} \quad (1)$$