

complex and have determined that the CPL associated with the Δ isomer is negative in sign for the ${}^5D_0 \rightarrow {}^7F_1$ Eu(III) transition.¹⁷

These results indicate that as long as the immediate symmetry of a Eu(III) complex is D_3 , a negative CPL band within the ${}^5D_0 \rightarrow {}^7F_1$ luminescence transition implies that the complex is the Δ isomer. We find that in the D_3 Eu(DPA)₃³⁻ complexes (assuming that the outer-sphere complexation does not greatly change the site symmetry about the lanthanide ion), a negative peak is observed at low pH. We now interpret these results to imply that the Δ isomer of the Eu(DPA)₃³⁻ complex is obtained in greater excess as a result of the Pfeiffer effects. One would naturally assume that the same isomer would be preferred in the analogous Tb(DPA)₃³⁻ complexes, and we therefore conclude that if the CPL of the ${}^5D_4 \rightarrow {}^7F_5$ Tb(III) transition is predominately negative, then one is observing the Δ isomer as well. For the few diaminocarboxylic acids that display the oppositely signed CPL at high pH, we conclude that it is the Λ isomer that is being produced in greater excess as a result of the outer-sphere complexation.

These conclusions enable a reevaluation of our previous results, which were presented elsewhere. We had previously found that addition of Λ -Cr(en)₃³⁺ to Tb(DPA)₃³⁻ led to the CPL having a predominantly negative sign.¹⁰ From the correlations just described, we now conclude that for this Pfeiffer-active system, the Λ enantiomer of the environmental substance enriches the Δ isomer of the Tb(III) complex. This observation provides further evidence that the Pfeiffer effect is not always a reliable means to determine the absolute configuration of a labile metal complex.¹⁹ In our study involving Pfeiffer optical activity induced by L-ascorbic acid,⁹ only negatively signed CPL was found, and we take this to imply that the Δ isomer was produced in this system. On the

other hand, the CPL produced when positive nitrogen atoms are incorporated in ring systems was always positive in sign,⁸ and this result implies that the Λ isomer was enriched in this system.

Conclusions

The work described in this paper has produced further evidence that Pfeiffer-type optical activity may be induced in 9-coordinate complexes of lanthanide ions, as well as in the better known 6-coordinate transition-metal complexes. The nature of the outer-sphere complexation is complex, but the bonding between the chelate and the chiral substrate appears to consist of a combination of hydrophobic and hydrogen-bonding forces. All the evidence presented in this and earlier works indicates that only the associative mechanism for the Pfeiffer effect can explain the experimental trends, and we have been able to use the CPL data in a quantitative manner as to obtain association constants for the outer-sphere complexes.

The variability in CPL sign patterns even for a single chiral substrate clearly demonstrates that general absolute configuration correlations must be made with extreme caution. We have found that the Δ isomer of Ln(DPA)₃³⁻ is enriched if bonding takes place at the aminocarboxylic functionality but the Λ enantiomer is preferred if bonding takes place elsewhere. The origins of these preferences are not presently clear, and further investigations are currently under way to attempt more general correlation rules.

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Kinetics of the Chelate Effect. Ring-Closing Reactions of *trans*-Dichloroammine[(2-aminoethyl)ammonium]platinum(II) Chloride and the (3-Aminopropyl)ammonium and (4-Aminobutyl)ammonium Analogues

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The kinetics of the ring-closing reaction of *trans*-[PtCl₂(NH₃)(N-NH)]⁺ [(N-NH) = (2-aminoethyl)ammonium (enH), (3-aminopropyl)ammonium (tnH), and (4-aminobutyl)ammonium (bnH)] have been studied in aqueous solution over a range of pH and temperature. The reaction takes the usual form



and the rate constants and activation parameters (k_{cl}^f at 30.0 °C/s⁻¹, ΔH^\ddagger (kcal mol⁻¹), ΔS^\ddagger /(cal K⁻¹ mol⁻¹)) for the en, tn, and bn complexes are 8.17, 12.1, -15; 0.62, 13.5, -15; and 0.0041, 16.1, -16, respectively. The acid dissociation constants, K'_a are 2.6×10^{-9} , 1.8×10^{-10} , and 3.9×10^{-11} mol dm⁻³, respectively, at 30.0 °C, $\mu = 2.0$. The marked dependence of rate constant on ring size arises from differences in ΔH^\ddagger rather than in ΔS^\ddagger whereas in analogous organic systems both contribute to the effect.

Introduction

In our studies of the effect of ring size on the kinetics of chelation we have used complexes containing the moderately strong *trans*-effect ligand, dimethyl sulfoxide, in order to facilitate ring opening.^{1,2} However, this also enhances the rate

of ring closing, and in the case of the smaller rings, we were unable to measure this rate unless the major part of the uncoordinated end of the diamine was rendered inactive by protonation. As a result it was not possible to separate the rate constant for ring closing (k_{cl}^f) from the acid dissociation

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Table I. Analytical Data

complex	empirical formula	% C		% H		% N		% Cl	
		calcd	found	calcd	found	calcd	found	calcd	found
Pt(en)Cl ₂	C ₂ H ₈ N ₂ Cl ₂ Pt	7.4	7.5	2.5	2.5	8.6	8.5		
Pt(tn)Cl ₂	C ₃ H ₁₀ N ₂ Cl ₂ Pt	10.6	10.5	3.0	2.8	8.2	8.1		
Pt(bn)Cl ₂	C ₄ H ₁₂ N ₂ Cl ₂ Pt	13.6	13.4	3.4	3.7	7.9	7.7		
Pt(ptn)Cl ₂	C ₅ H ₁₄ N ₂ Cl ₂ Pt	16.3	16.3	3.8	4.0	7.6	7.5		
Pt(1,2-dac)Cl ₂	C ₆ H ₁₄ N ₂ Cl ₂ Pt	19.0	18.8	3.7	3.8	7.4	7.2		
Pt(1,3-dac)Cl ₂	C ₆ H ₁₄ N ₂ Cl ₂ Pt	19.0	18.7	3.7	3.9	7.4	7.2		
Pt(Me ₄ en)Cl ₂	C ₆ H ₁₆ N ₂ Cl ₂ Pt	18.9	18.9	4.2	4.4	7.3	7.6		
[Pt(en)(NH ₃) ₂]Cl ₂	C ₂ H ₁₄ N ₄ Cl ₂ Pt	6.7	6.7	3.9	3.9	15.6	15.4		
[Pt(tn)(NH ₃) ₂]Cl ₂	C ₃ H ₁₆ N ₄ Cl ₂ Pt	9.6	9.5	4.3	4.3	15.0	15.0		
[Pt(bn)(NH ₃) ₂]Cl ₂	C ₄ H ₁₈ N ₄ Cl ₂ Pt	12.3	12.0	4.6	4.7	14.4	14.0		
[Pt(1,2-dac)(NH ₃) ₂]Cl ₂	C ₆ H ₂₀ N ₄ Cl ₂ Pt	17.4	17.3	4.9	5.0	13.5	13.4		
[Pt(1,3-dac)(NH ₃) ₂]Cl ₂	C ₆ H ₂₀ N ₄ Cl ₂ Pt	17.4	17.0	4.9	4.9	13.5	13.2		
<i>trans</i> -[Pt(NH ₃)(enH)Cl ₂]Cl	C ₂ H ₁₂ N ₃ Cl ₃ Pt	6.3	6.4	3.2	3.1	11.0	11.0	28.0	27.6
<i>trans</i> -[Pt(NH ₃)(tnH)Cl ₂]Cl	C ₃ H ₁₄ N ₃ Cl ₃ Pt	9.2	9.0	3.6	3.7	10.7	10.5	27.0	27.0
<i>trans</i> -[Pt(NH ₃)(bnH)Cl ₂]Cl	C ₄ H ₁₆ N ₃ Cl ₃ Pt	11.8	11.8	4.0	4.0	10.3	10.3	26.1	26.0
[Pt(NH ₃)(en)Cl]Cl	C ₂ H ₁₁ N ₃ Cl ₂ Pt	7.0	6.9	3.2	3.2	12.3	12.1	21.0	20.9

constant of the protonated amine (K_a'). Although we could estimate a reasonable value for K_a' and hence an approximate value for k_{Cl}^f , such data were not precise enough to allow study of the temperature dependence of k_{Cl}^f in order to determine the activation parameters. The classic work of Carter and Beattie³ showed that it was possible to obtain the full analysis of the ring-closure processes of *trans*-[PtCl₂(enH)₂]²⁺, and in a brief communication, Mønsted and Bjerrum⁴ reported the acid-dependent rate constants for the ring-closing reactions of *trans*-[PtCl₂(NH₃)(enH)]⁺ and *trans*-[PtCl₂(NH₃)(tnH)]⁺ but did not separate k_{Cl}^f from K_a' . We have reexamined these reactions and extended our studies to basic solutions and also to the complex *trans*-[PtCl₂(NH₃)(bnH)]⁺, and the kinetics and activation parameters are reported in this paper.

Experimental Section

Materials. *trans*-Dichloroamine[(aminoethyl)ammonium]platinum(II) chloride was prepared by a modification of Drew's method.⁵ [Pt(NH₃)₂(en)]Cl₂ (1.8 g, 5.0 mmol) was refluxed in concentrated hydrochloric acid (20 cm³) for 8 h at 100 °C. As the solution cooled, bright yellow crystals separated and were filtered off, washed with acetone and ether, and dried.

***trans*-Dichloroamine[(3-aminopropyl)ammonium]platinum(II) Chloride.** [Pt(NH₃)₂(tn)]Cl₂⁶ (1.9 g) was dissolved in 6 M hydrochloric acid (25 cm³) and the solution heated in a sealed glass tube at 120 °C for 8 h. The solution was then concentrated on a rotary evaporator and the product precipitated by adding acetone and ether. The material was contaminated with starting material and required several recrystallizations from concentrated hydrochloric acid before it was pure.

***trans*-Dichloroamine[(4-aminobutyl)ammonium]platinum(II) chloride** was prepared from [Pt(NH₃)₂(bn)]Cl₂ in a similar manner, the reaction requiring only 6 h in a sealed tube at 120 °C.

Dichloro(1,4-diaminobutane)platinum(II). [Pt(Me₂SO)(bn)Cl]Cl, prepared by the method of Romeo et al.,⁷ was boiled with a saturated aqueous solution of sodium chloride until the required pale yellow complex separated. This was filtered off and washed with large amounts of cold water to remove the sodium chloride, then with ethanol, and finally with ether. It was dried under vacuum.

Diammine(1,4-diaminobutane)platinum(II) Chloride. [Pt(bn)Cl₂] was suspended in aqueous ammonia and allowed to stand until all had dissolved. The solution was filtered and evaporated to a small volume, and the complex was precipitated by the careful addition of acetone and then ether, filtered off, washed with acetone and ether, and dried under vacuum.

***trans*-Chloroamine(1,2-diaminoethane)platinum(II) Chloride.** *trans*-[Pt(NH₃)(enH)Cl₂]Cl (0.3 g, 0.8 mmol) was suspended in

methanol (30 cm³) and carefully neutralized by the slow addition of dilute aqueous sodium hydroxide solution. The solution was filtered immediately and reduced to small volume in a rotary evaporator. On addition of acetone and ether a white precipitate separated and was filtered off, washed with ether, and dried under vacuum.

Compounds of the type Pt(N-N)Cl₂, where N-N = 1,2-diaminoethane, 1,3-diaminopropane, *trans*-1,2-diaminocyclohexane, *cis*-1,3-diaminocyclohexane, 1,5-diaminopentane, and *N,N,N',N'*-tetramethyl(1,2-diaminoethane), were prepared by reacting the appropriate amine with K₂PtCl₄ in aqueous solution according to Drew's method⁵ and could be converted to [Pt(N-N)(NH₃)₂]Cl₂ by reaction with diluted ammonia as described by Drew and Tress.⁶

1,3-Diaminocyclohexane was kindly provided by C. J. Cooksey, and other materials were AR grade where possible. The amines were purchased from Aldrich Chemical Co. and purified by vacuum distillation after first being refluxed over NaOH pellets.

Buffer Solutions. The buffers were prepared from aqueous solutions of AR NaH₂PO₄, Na₂HPO₄, B(OH)₃, and NaOH by standard methods.^{8,9} Further details are given in the relevant tables. The pH was determined before each experiment with a Radiometer PHM-26 pH meter that had been calibrated with standard borax (pH 9.14 at 30.0 °C) and potassium hydrogen phthalate (pH 4.02 at 30.0 °C) and checked against an equimolar solution of NaH₂PO₄ and Na₂HPO₄ (pH 6.85 at 30.0 °C). The saturated KCl solution in the standard calomel electrode was replaced by 4 M NaCl to avoid precipitation of KClO₄ when this was inserted in the NaClO₄ containing buffer solutions.

Kinetics. The reactions with $t_{1/2} < 20$ s were followed by using a Durrum D110 stopped-flow spectrophotometer incorporating a Durrum D131 photometric log amplifier and a Tektronix storage oscilloscope (Type 464B). For reactions of $t_{1/2} > 1$ s the output from the photon multiplier was connected to the y axis of a Servoscribe RE 511-20 potentiometric recorder, and for faster reactions the output was first stored in a Datalab DL 905 transient recorder and then transferred to the pen recorder. Reactions were initiated by mixing equal volumes of solutions containing the Pt(II) complex (acidified to 0.01 M with HCl) and 0.2 M NaOH, both solutions being 1 M with respect to NaCl and $\mu = 2.0$ (NaClO₄). The slow reactions were initiated by adding a known mass of complex to 3.0 cm³ of the solution containing the rest of the reagents previously brought to the reaction temperature in the thermostated spectrophotometer cell. Preliminary multiple-scanning experiments using a Unicam SP 800 spectrophotometer were used to characterize the reaction and to choose the optimum wavelength (310 nm) for the kinetics study, which was carried out with a Unicam SP 1750 spectrophotometer in the single-wavelength mode.

Results

The formation of complexes of the type [Pt(N-N)Cl₂] by reacting an aqueous solution of K₂PtCl₄ with the diamine

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(N-N) according to the method of Drew^{5,6} was successful for N-N = 1,2-diaminoethane (en), 1,3-diaminopropane (tn), *trans*-1,2-diaminocyclohexane (1,2-dac), *cis*-1,3-diaminocyclohexane (1,3-dac), and *N,N,N',N'*-tetramethyl-1,2-diaminoethane (Me₄en), and apparently so for 1,5-diaminopentane (pe). However, in the last case, the yellow compound obtained, although analyzing correctly for Pt(pe)Cl₂, was insoluble in water and the usual solvents and did not react with ammonia or dimethyl sulfoxide. In the $\nu_{\text{Pt-Cl}}$ region the IR spectrum of this complex has a very broad band centered at 322 cm⁻¹ whereas those of the others have two resolved peaks in the range 330–310 cm⁻¹, characteristic of *cis*-[PtCl₂(am)₂] complexes.¹⁰ It is therefore probable that the "Pt(pe)Cl₂" complex is polymeric, with the diamine acting as a bridging ligand rather than as a chelate. Drew⁶ reported that the complex with 1,4-diaminobutane (bn) was a hygroscopic, and yet water-insoluble, material, and although it was possible with care to obtain low yields of the genuine monomeric [Pt(bn)Cl₂] complex by a modification of Drew's method in which the reaction mixture was brought to pH 2 by adding hydrochloric acid, it was more convenient to make this complex by the reaction between the known, chelated, [Pt(bn)(Me₂SO)Cl]Cl⁷ and excess NaCl in aqueous solution. All attempts to make monomeric [Pt(pe)Cl₂] were unsuccessful. All of the dichloro complexes could be converted to the cationic diammine derivatives [Pt(N-N)(NH₃)₂]Cl₂ by reaction with aqueous ammonia, but the subsequent reaction with hydrochloric acid to give *trans*-[Pt(N-NH)(NH₃)Cl₂]Cl as reported by Drew was only successful in the cases where N-N = en, tn, and bn. When N-N was 1,2-dac and 1,3-dac, only unreacted material could be recovered in spite of heating the complexes in concentrated hydrochloric acid in sealed tubes for considerable periods of time at high temperatures. The complexes containing the protonated monodentate diamines have sharp single peaks in the $\nu_{\text{Pt-Cl}}$ region of their infrared spectra (335, 331, and 338 cm⁻¹ for the enH, tnH, and bnH complexes, respectively), consistent with their formulation as *trans*-dichloro complexes.

Preliminary spectrophotometric studies indicated that these complexes remain unchanged for very long periods of time in acid aqueous solutions (pH 0) but that at pH > 2, the spectra change to those of the chelated [Pt(N-N)(NH₃)Cl]⁺ cation at rates that are dependent upon the pH and the nature of N-N. Comparison was made with an independently prepared and characterized sample of [Pt(en)(NH₃)Cl]Cl. The spectral change is characterized by two good isosbestic points (295 and 243 nm for N-N = en, 274 and 243 nm for tn, and 272 and 243 nm for bn), indicating the absence of any significant amount of any intermediate.

The conditions used to study the slow ring closing in buffered solutions depended upon the nature of N-N. The closing of the five-membered ring was studied over the pH range 4–6, which was conveniently attained by using phosphate buffers, independently shown not to interfere with the reaction. The closing of the six-membered ring was studied over the pH range 6.5–8.0 by using boric acid–sodium hydroxide buffers, while the very slow closing of the seven-membered ring was also studied in this buffer medium, but owing to the need to keep [H⁺] >> K_a' (the acid dissociation constant of the protonated monocoordinated diamine) in order to simplify the kinetics, this had to be restricted to a narrower pH range, 8.2–8.8. So that these results could be compared with those obtained on other systems, the reactions were studied in the presence of 1.0 M NaCl even though preequilibrium solvolysis did not complicate the kinetics of these systems. The ionic strength was maintained at $\mu = 2.0$ with NaClO₄. Reactions

Table II. Rate Constants for the Reaction
trans-[Pt(NH₃)(NH₂(CH₂)_nNH₂)Cl₂] →
[Pt(NH₃)(NH₂(CH₂)_nNH₂)Cl]⁺ + Cl^{-a}

<i>n</i>	temp/°C	<i>k</i> _{obsd} /s ⁻¹	ΔH^\ddagger / (kcal mol ⁻¹)	ΔS^\ddagger / (cal K ⁻¹ mol ⁻¹)
2	16.5	2.73		
	20.0	3.40		
	25.0	4.65		
	30.0	8.17		
	35.0	11.3		
	40.0	12.7		
3	45.0	19.5	12.1 ± 0.7	-14.6 ± 2.3
	15.0	0.190		
	20.0	0.291		
	25.0	0.426		
	30.0	0.623		
	35.0	0.90		
4	40.0	1.20		
	45.0	2.14	13.5 ± 0.5	-15.0 ± 1.7
	15.0	0.00088		
	20.0	0.00153		
	25.0	0.00250		
	30.0	0.00409		
4	30.0	0.00380 ^b		
	30.0	0.00396 ^c		
	35.0	0.00622		
	40.0	0.00889	16.1 ± 0.4	-16.7 ± 1.3

^a In water; [NaCl] = 1.0 M; [NaOH] = 0.1 M; $\mu = 2.0$ (NaClO₄); [complex] = 2.0 × 10⁻³ M; measured at 310 nm. ^b 0.20 M NaOH. ^c [complex] = 4.0 × 10⁻³ M.

Table III. Rate Constants for the Reaction
trans-[Pt(NH₃)(NH₂(CH₂)_nNH₂)Cl₂]⁺ →
[Pt(NH₃)(NH₂(CH₂)_nNH₂)Cl]⁺ + H⁺ + Cl⁻ in Buffer^a

<i>n</i>	C _S /C _H ^b	X ^c	X' ^d	pH	10 ⁶ a _H ⁺	10 ⁴ × <i>k</i> _{obsd} /s ⁻¹
2	0.094			4.569	27.0	7.1
	0.14			4.792	16.1	13.0
	0.23			5.038	9.16	21.4
	0.36			5.246	5.68	37.4
	0.96			5.682	2.08	103
	1.56			5.926	1.19	173
3		1.19		6.915	0.122	12.9
		1.80		7.160	0.069	18.8
		2.68		7.331	0.0467	23.8
		3.86		7.549	0.0283	39.8
		7.41		7.996	0.0101	107
4			6.06	8.280	0.00525	0.480
			6.75	8.394	0.00404	0.552
			7.41	8.488	0.00325	0.654
			8.08	8.580	0.00263	0.808
			8.70	8.660	0.00219	0.854
			9.30	8.776	0.00168	1.13

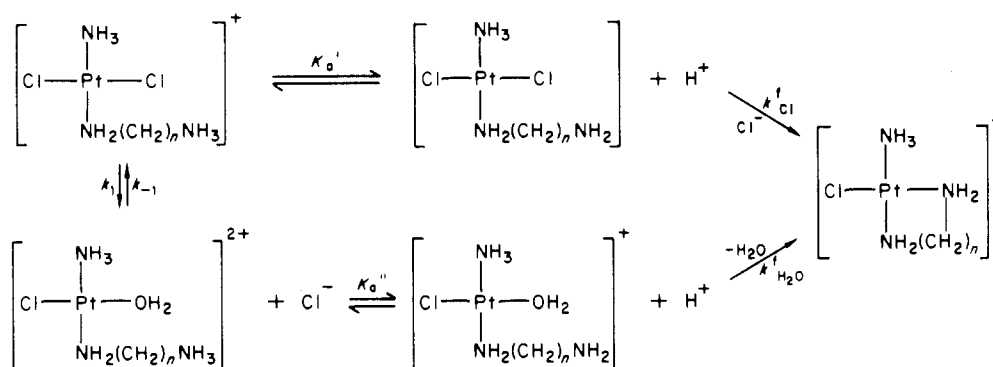
^a In water at 30.0 °C; [NaCl] = 1.0 M; $\mu = 2.0$ (NaClO₄); [complex] = 2.0 × 10⁻³ M; measured at 310 nm. ^b C_H = [NaH₂PO₄]; C_S = [Na₂HPO₄]; C_H + C_S = 0.10 M. ^c Buffer made up with 25.0 cm³ of 0.10 M boric acid + X cm³ of 0.110 M NaOH made up to 50.0 cm³. ^d Buffer made up with 25.0 cm³ of 0.10 M boric acid + X' cm³ of 0.200 M NaOH made up to 50.0 cm³.

were carried out at 30.0 °C with a total buffer concentration (0.10 M) large enough to ensure first-order kinetics in any run. Good semilogarithmic plots of ln(A_t - A_∞) vs. time (A_t and A_∞ being the absorbances of the reaction mixture at time *t* and at the end of the reaction, respectively) were obtained. The values of *k*_{obsd} are collected in Table III. Plots of the experimental first-order rate constant (*k*_{obsd}) vs. [H⁺]⁻¹ gave good straight lines, and the slopes and intercepts obtained by a linear least-squares analysis are also given.

As the pH increases the simple inverse [H⁺] dependence is lost, and in the presence of sufficient base (pH > 12) [H⁺] << K_a' and the rate of ring closing becomes independent of pH. In the case of the en and tn species the reactions were

(10) F. R. Hartley, "The Chemistry of Platinum and Palladium", Applied Science Publishers, London, 1973, p 242.

Scheme I



too fast to be followed by the conventional techniques and required a stopped-flow spectrophotometer. The complexes were provided as solutions of *trans*-[Pt(NH₃)(N-NH)Cl₂]Cl (4×10^{-3} M) in water containing HCl (0.01 M) and NaCl (1.0 M) brought to $\mu = 2.0$ (NaClO₄), and the reaction was initiated by mixing this with an equal volume of sodium hydroxide solution (0.20 M) in 1.0 M NaCl at $\mu = 2.0$ (NaClO₄). In the absence of rapid-scanning equipment it was only possible to follow the reaction at a single wavelength. The reaction of the bn complex under these conditions was slow enough to be followed in a normal spectrophotometer, and the reaction was initiated by adding a weighed amount of *trans*-[Pt(NH₃)(bnH)Cl₂]Cl to a solution containing NaOH (0.10 M) and NaCl (1.0 M) at $\mu = 2.0$ (NaClO₄), which has previously been brought to the reaction temperature in the thermostated spectrophotometer cell. However, it was not slow enough to permit repetitive scanning, and so no information about isobestic points is available. The spectra at the end of the reactions were all consistent with those expected for the chelated product. The reactions were studied over a range of temperatures, and the rate constants, obtained in the usual way, are collected in Table II.

Discussion

The kinetics of the ring-closing reaction are fully consistent with the mechanism (Scheme I) discussed in detail elsewhere.¹⁻³ If we ignore the solvolysis of the substrate, which played a major part in determining the chloride ion dependence of the rates of ring closing of *cis*-[Pt(Me₂SO)(N-NH)Cl₂]⁺,^{1,2} and if the reaction goes to completion, the rate law simplifies to $k_{\text{obsd}} = k_{\text{Cl}}^f K_a' (K_a' + [\text{H}^+])^{-1}$, where k_{obsd} is the measured rate constant for the pseudo-first-order process that occurs if $[\text{H}^+]$ remains constant during the run. Except at the very highest concentrations of H^+ used, which will be discussed below, this approximation is justified.

The studies were carried out in two separate regions of pH: first, where $[\text{H}^+] \ll K_a'$, where the substrate is almost entirely in the form of the unprotonated species and the expression reduces to $k_{\text{obsd}} = k_{\text{Cl}}^f$, and second, where $[\text{H}^+] \gg K_a'$, in which case the relationship $k_{\text{obsd}} = k_{\text{Cl}}^f K_a' [\text{H}^+]^{-1}$ should hold. The first region allows a direct determination of k_{Cl}^f , which does not depend upon the accuracy with which the pH is determined and which does not require an estimate of K_a' . When the information from the two regions is combined, it is possible to determine K_a' with some measure of reliability.

Preliminary experiments at pH >12 showed that the rate of ring closing was independent of pH, and the rate constants were then determined accurately in the presence of 0.1 M NaOH solution. In the buffered solutions, where $[\text{H}^+] \gg K_a'$, the predicted inverse $[\text{H}^+]$ dependence was observed, but in the case of the tnH and bnH complexes there is a finite intercept at $[\text{H}^+]^{-1} = 0$ [$(3.06 \pm 0.86) \times 10^{-4} \text{ s}^{-1}$ and $(1.60 \pm 0.37) \times 10^{-5} \text{ s}^{-1}$ for the tnH and bnH complexes, respectively]. An acid-independent contribution of these orders of

magnitude in the enH complex would have been masked by the much greater acid-dependent contribution. Such intercepts have been observed elsewhere, as for example, in the closing of the seven-membered ring of *cis*-[Pt(Me₂SO)(bnH)Cl₂]⁺² and in the closing of the five-membered ring of [Pt(enH)-Cl]²⁺.³ The explanations offered in the two cases differ. In the first the intercept was assigned to the reversibility of the ring-formation process and shown to be equal in magnitude to the independently measured rate constant for ring opening, while in the second case it was assigned to a solvolytic pathway for ring closing. In the case of the *trans*-[Pt(NH₃)(N-NH)Cl₂]⁺ complexes the ring-opening reaction does not appear to be fast enough to account for the acid-independent term, while the solvolytic rate constant would not be expected to be dependent on the size of the incipient ring. The value for the tnH complex, $3.1 \times 10^{-4} \text{ s}^{-1}$ at 30.0 °C, is of the magnitude expected (e.g., k_1 for substitution in *trans*-[Pt(NH₃)₂Cl₂] in water at 25 °C is $9.8 \times 10^{-5} \text{ s}^{-1}$), although the *cis* effect resulting from the replacement of ammonia by a more basic primary amine might have been expected to have reduced the reactivity slightly.¹² However, the value of the intercept for bnH, $= 1.6 \times 10^{-5} \text{ s}^{-1}$ at 30.0 °C, is too small by at least 1 order of magnitude. If the solvolytic pathway is to make a significant contribution to the kinetics, it is necessary for the displacement of water by the free end of the diamine to be much more probable than its displacement by chloride. This may well be possible in the tn complex, but if the 10²-fold decrease in reactivity for the ring closing by the displacement of chloride is also mirrored in the displacement of water, then on going from tn to bn it is possible that the balance is tipped in favor of the displacement of water by chloride and the intercept is much reduced by mass-law retardation. Whatever the cause of the acid-independent intercept, it makes only a small contribution to the rate of ring closing for the tnH complex and does not affect the value of the slope significantly. The mass-law retardation by chloride in the case of the bnH complex would lead to the plot of k_{obsd} vs. $[\text{H}^+]^{-1}$ being curved at low values of $[\text{H}^+]^{-1}$, and the linear least-squares-determined slope would be greater than $k_{\text{Cl}}^f K_a'$. However, the data are randomly scattered about this line, and there is no indication of any systematic curvature in this plot. Nevertheless, it should be borne in mind when estimating the value of k_a' by dividing this slope by the independently determined value of k_{Cl}^f that the true value of K_a' could be somewhat smaller than the value quoted.

The direct measurement of k_{Cl}^f in alkaline solution is not complicated by these problems, and the obtained values indicate that, as in other systems, the rate constants decrease as the size of the rings formed increase. At 30.0 °C the relative

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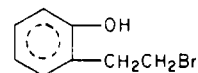
Table IV. Summary of Rate Constants, Activation Parameters, and Effective Molarities for the Ring-Closing Processes and Other Relevant Data

	ring size		
	5	6	7
k_{Cl}^{\ddagger} at 30.0 °C/s ⁻¹	8.17	0.623	0.00409
ΔH^{\ddagger} /(kcal mol ⁻¹)	12.1	13.5	16.1
ΔS^{\ddagger} /(cal K ⁻¹ mol ⁻¹)	-15	-15	-17
$k_{\text{Cl}}^{\ddagger}K_{\text{a}}^{\prime}/(\text{M s}^{-1})$	2.06×10^{-8} ^a	1.05×10^{-10} ^a	1.60×10^{-13}
$K_{\text{a}}^{\prime}/\text{M}$	2.52×10^{-9}	1.69×10^{-10}	3.91×10^{-11}
pK_{a}^{\prime}	8.60	9.77	10.41
effective molarity/M ^b	1010	77	0.505

^a Monsted and Bjerrum⁴ quote 7×10^{-9} and 7×10^{-11} M s⁻¹ for the en and tn complexes, respectively, at 25.0 °C. ^b Obtained by using the rate constant for the reaction $\text{trans-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2] + \text{NH}_3 \rightarrow [\text{Pt}(\text{NH}_3)_3\text{Cl}]^+ + \text{Cl}^-$ as standard. Recalculation of data in ref 13 gives $k_2 = 8.1 \times 10^{-3}$ M⁻¹ s⁻¹ at 30.0 °C, $\Delta H^{\ddagger} = 10.4 \pm 1.0$ kcal mol⁻¹, and $\Delta S^{\ddagger} = -34 \pm 4$ cal K⁻¹ mol⁻¹.

magnitudes of the rate constants are in the ratio $2 \times 10^3:1.5 \times 10^2:1$ for the formation of the five-, six-, and seven-membered rings, respectively, and are to be compared with the ratios $4 \times 10^2:1 \times 10^2:1$ estimated for the corresponding *cis*-[Pt(Me₂SO)(N-N)Cl₂] species.^{2,23} It must, however, be borne in mind that the values deduced for the closing of the five- and six-membered rings depend on the accuracy of the estimation of the acid dissociation constant K_{a}^{\prime} , and the magnitude of uncertainty is probably greater than the observed differences. The most important observation is that the reactivity differences in the *trans*-[Pt(NH₃)(N-N)Cl₂] series arise from an increase in the enthalpy of activation rather than a decrease in the entropy of activation. This is the first time that there has been a direct comparison of the three ring sizes in the same series of complexes, although comparisons have been made of five- and six-membered ring closing. For example, Rotondo¹³ finds that the 4-fold decrease in rate on changing from $n = 2$ to $n = 3$ in the ring-closing reactions of $[\text{Pt}(\text{bpy})(\text{NH}_2(\text{CH}_2)_n\text{OH})\text{Cl}]^+$ is due entirely to a decrease in the entropy of activation, but in this system there has not been a clear identification of the processes to which the rate constants relate. The observation in our case that the reactivity differences are associated with changes in the enthalpies of activation is of considerable importance in any discussion that introduces the concept of "effective molarity". It is not possible to compare rate constants for the closing of a chelate ring with those for the entry of a monodentate amine, all other factors being equal, because the two constants are of different kinetic order. The ratio $k_{\text{Cl}}^{\ddagger}(\text{ring closing})/k_{\text{Cl}}^{\ddagger}(\text{monodentate})$ has the dimensions of concentration and, formally at least, is the concentration that the independent nucleophile must achieve in order that the reaction has the same first-order rate constant as ring closing. This quantity, termed the "effective molarity" or the "effective concentration", can be of a magnitude that has no physical reality. In the discussion of the rates of ring closing of *cis*-[Pt(Me₂SO)(N-N)Cl₂]² an attempt was made to estimate values for $k_{\text{Cl}}^{\ddagger}(\text{monodentate})$ by using known relationships for the dependence of the rate constant on the basicities of the entering amine and the amine *cis* to the leaving group. No equivalent study has been made of the dependence of rate constants on amine basicity in the reactions of the type *trans*-[Pt(NH₃)(am)Cl₂] + am' → *trans*-[Pt(NH₃)(am)(am')Cl]⁺ + Cl⁻, and so we have used as our standard the rate constant for the reaction where am = am' = NH₃, interpolated from the data of Martin et al.¹⁴ (8.1×10^{-3} M⁻¹ s⁻¹). Since the amines used are all somewhat more basic than ammonia, this value is probably larger than the correct value, but the

discrepancy is unlikely to be large, and in any case the differences are much less than the differences in the rate constants for the closing of the rings of different size.¹⁵ There has been extensive discussion of the concept of effective molarity and its dependence on ring size in the literature,^{16,17} and although it has been applied from time to time to the formation of transition-metal chelates, no study has gone beyond the formation of a seven-membered ring. No such constraint applies to the formation of organic rings, and the variation of rate constants and activation parameters with ring size has been studied from 3-membered rings to 33-membered rings.^{18,19} The largest values for effective molarity are found in the closing of five-membered rings; for example, in the cyclic etherization of



the effective molarity is 1.3×10^5 M.¹⁸ This is some 2 orders of magnitude greater than the effective molarities associated with the closing of five-membered chelate rings at platinum(II). The decrease in the effective molarity on going from five- to six-membered rings (factors between 30 and 200) is generally much more marked in these cases than that found for d⁸ metal centers, where the factor is ≤ 10 . As the ring size of the organic product increases, there is a further decrease in the effective molarity of the nucleophile that levels off to an approximately constant value by the time a ten-membered ring is reached. In the case of lactone-forming reactions of $\omega\text{-Br}(\text{CH}_2)_n\text{COOH}$,²⁰ the formation of three- and four-membered rings can also be studied. The maximum effective molarity is associated with the formation of the five-membered ring, although this is much smaller than that found in the other organic cases (1.6×10^3 M) and comparable in magnitude to those found in the Pt(II) systems. In the case of the two Pt(II) complexes where the formation of a seven-membered ring can be studied, there is a 10²-fold decrease in effective molarity on going from a six- to a seven-membered ring, similar to that observed in the formation of cyclic ethers. In spite of much effort we have been unable to prepare inorganic complexes with large enough bidentate ligands to examine the closing of eight- or greater-membered rings. An indirect study, which is reported elsewhere, indicates that the closing of the eight-membered ring in *trans*-[Pt(Me₂SO)(N-N)Cl₂] (N-N = monodentate 1,5-diaminopentane) is at least 10² times slower than the closing of the seven-membered ring when N-N = 1,4-diaminobutane.²¹ In the formation of cyclic ethers^{18,19} it was shown that the decrease in the rate of ring closure with increasing ring size was associated with a decrease of ΔS^{\ddagger} , there being a linear relationship between ΔS^{\ddagger} and the size of the ring (in the range five to ten membered) with about 4 cal K⁻¹ mol⁻¹ per unit of ring size,¹⁸ but the effect tails off with greater ring sizes.¹⁹ The enthalpies of activation show less of a systematic trend although there is a tendency for them to rise to a maximum for the formation of eight- to nine-membered rings and then decrease. Part of this behavior has been ascribed to ring strain. In the ring-closing reactions of *trans*-[Pt(NH₃)(N-N)Cl₂], the entropies of activation remain

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- (15) If we use the parameters that apply to the Me₂SO complex, the calculated values for $k_{\text{Cl}}^{\ddagger}(\text{monodentate})$ are 6.2×10^{-3} , 5.0×10^{-3} , and 4.7×10^{-3} M⁻¹ s⁻¹ for the en, tn, and bn complexes, respectively.
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reasonably constant over the narrow range of ring size studied (five to seven), and the very large differences in the rate constants comes mainly from changes in ΔH^\ddagger . The major changes in ΔS^\ddagger are observed on going from the intermolecular reaction [$\Delta S^\ddagger = -34 \text{ cal K}^{-1} \text{ mol}^{-1}$ for the reaction between *trans*-[Pt(NH₃)₂Cl₂] and NH₃¹³] to the intramolecular process [$\Delta S^\ddagger = -15$ to $-16 \text{ cal K}^{-1} \text{ mol}^{-1}$]. It has previously been suggested that, in the closing of the five-membered ring, the ground state of the reagents already corresponds to a position well along the reaction coordinate of the intermolecular process to the point where the adjustment of the solvation of the interacting species is well advanced;¹ to what extent does the longer chain length between the functional groups in the tn and bn complexes reduce this "prearrangement"? Some years ago Cotton and Harris²² calculated the probability of finding the second amino group of a monocoordinated diamine within the region 1.6–2.0 Å of the metal ion and showed that it did not vary greatly on going along the series 1,2-diaminoethane to 1,5-diaminopropane. They concluded that this consideration would therefore make only a small and fairly constant contribution to the entropy change associated with cyclization and calculated that the different losses of entropy associated with closing rings of different sizes arose from the differing conformational restrictions on closing the rings. The four-coordinate planar d⁸ complexes are, in principle, coordinately unsaturated, and the possibility of loose coordination in the axial position will greatly increase the probability of finding the free end of the diamine in the vicinity of the Pt(II). The

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Monte Carlo or random walk treatment will greatly underestimate this probability. The weak coordination will also serve to close the ring loosely so that the changes of entropy due to conformational restrictions will have occurred in the ground state and therefore will not appear in the entropy of activation. Such incipient chelation is an alternative way of viewing the suggestion made above that the ring-closing process starts from a position some way along the reaction coordinate that is appropriate for the intermolecular process. Once the ring size becomes large enough for only a small fraction of the substrate to be incipiently chelated at any time, it is likely that the entropies of activation will decrease with increasing ring size in the way observed elsewhere. The tightening of the ring as the NH₂ group becomes more tightly bound to the Pt will lead to ring strain and interatomic repulsions, and these will result in an increase in the enthalpy of activation as ring size increases. In the range of ring size covered by this work it is suggested that this is the main cause of the decrease in the rate of ring closing. The organic ring closing reactions do not have the benefit of incipient chelation in the noncyclic substrate since the carbon is coordinately saturated.

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Registry No. *trans*-[Pt(NH₃)(NH₂(CH₂)₂NH₂)Cl₂], 80243-17-0; *trans*-[Pt(NH₃)(NH₂(CH₂)₃NH₂)Cl₂], 80243-18-1; *trans*-[Pt(NH₃)(NH₂(CH₂)₄NH₂)Cl₂], 80243-19-2; *trans*-[Pt(NH₃)(NH₂(CH₂)₂NH₃)Cl₂]⁺, 80243-20-5; *trans*-[Pt(NH₃)(NH₂(CH₂)₃NH₃)Cl₂]⁺, 80243-21-6; *trans*-[Pt(NH₃)(NH₂(CH₂)₄NH₃)Cl₂]⁺, 80243-22-7; Pt(pe)Cl₂, 80243-50-1.

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Apical Interactions in Copper(II) Complexes. Stability and Structure of the Binary and Ternary Copper(II) Complexes Formed with L-Alaninamide and Diethylenetriamine in Aqueous Solution¹

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By potentiometric pH titrations the stability constants were determined in aqueous solutions of the binary parent and mixed-ligand complexes formed in systems containing L-alaninamide (AlaA), diethylenetriamine (dien), and Cu²⁺. In contrast to an earlier claim, where for the species Cu(dien)(AlaA-H)⁺ an apical coordination of the ionized amide nitrogen was suggested, in the present work this deprotonated ternary complex could not even be detected. All experimental data could be perfectly fitted by assuming the species Cu(AlaA)₂²⁺, Cu(AlaA)₂²⁺, Cu(AlaA-H)⁺, Cu(AlaA)(AlaA-H)⁺, Cu(AlaA-H)₂, Cu(dien)₂²⁺, Cu(dien)(OH)⁺, Cu(dien)(H-dien)³⁺, Cu(dien)₂²⁺, and Cu(dien)(AlaA)₂²⁺. These results were confirmed by spectrophotometric measurements, and the spectral characteristics (λ_{max} and extinction coefficient) were determined. By comparisons with literature data it becomes evident, in agreement with earlier conclusions, that in Cu(dien)(H-dien)³⁺ four amino nitrogens are equatorially coordinated while one N interacts apically; in Cu(dien)₂²⁺ clearly all six nitrogens participate in complex formation; i.e., two nitrogens interact apically. For Cu(dien)(AlaA)₂²⁺ there is evidence that four nitrogens are equatorially coordinated and that the carbonyl oxygen of AlaA interacts to a significant extent with an apical position of Cu²⁺. Regarding biological systems two important conclusions may be drawn from this and related work: (i) An apical coordination of amino nitrogens or of oxygen donors to Cu²⁺ is easily achieved in the physiological pH range, while there is no such evidence for the coordination of an ionized amide nitrogen. (ii) In a mixed-ligand complex an ionized amide group may be formed and coordinated only if two equatorial coordination positions of Cu²⁺ are accessible, namely, for the terminal amino nitrogen and the neighboring ionized amide nitrogen of the "peptide" ligand.

The ionized amide residue is an important ligating group in low molecular weight Cu²⁺ peptide complexes.⁴ The same

type of coordination is also known to occur in nature, e.g., in human serum albumin;^{5,6} similarly, the antibiotic bleomycin is most probably active via metal ion complexes and the one

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