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Kinetics of the Chelate Effect. Ring Closing and Ring Opening in *cis*-Dichloro(dimethyl sulfoxide)((3-aminopropyl)ammonium)- and -((4-aminobutyl)ammonium)platinum(II) Chloride. Effect of Ring Size

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Received December 29, 1977

The kinetics of the reaction *cis*-$[Pt(dmso)(N\text{-}NH)Cl_2]^+ \rightleftarrows [Pt(dmso)(N\text{-}N)Cl]^+ + H^+ + Cl^-$ (dmso = S-bonded dimethyl sulfoxide; N-N = chelated 1,3-diaminopropane or 1,4-diaminobutane; N-NH = the protonated monodentate form of the diamine) have been studied in both directions in aqueous solution at 30.0 °C, using phosphate buffers where necessary. The mechanism is identical with that established for the 1,2-diaminoethane complex which, for ring closing, involves a rapid reversible solvolysis of the chloride trans to the dimethyl sulfoxide, equilibrium constant K_{Cl}, and rapid acid–base equilibria between the protonated and unprotonated forms of the amine (equilibrium constants K_a' and K_a'' for the chloro and aquo complexes, respectively), followed by a rapid first-order ring closing of the unprotonated species, rate constants k^f_{Cl} and $k^f_{H_2O}$. In the case of the 1,4-diaminobutane complex, k^f_{Cl} could be measured directly in alkaline solution. For the 1,3-diaminopropane complex (μ = 2.0, $NaClO_4$), $K_{Cl} = (4.4 \pm 0.8) \times 10^{-4}$ M, $K_a'k^f_{Cl} = (1.01 \pm 0.07) \times 10^{-6}$ M s^{-1}, and $K_a''k^f_{H_2O} = (3.0 \pm 0.7) \times 10^{-5}$ M s^{-1}, while for the 1,4-diaminobutane complex (μ = 1.2, $NaClO_4$) $K_a'k^f_{Cl} = (2.13 \pm 0.02) \times 10^{-9}$ M s^{-1} and k^f_{Cl} = 22.3 s^{-1} (all at 30 °C). Temperature variation studies of k^f_{Cl} give $\Delta H^\ddagger = 9.80 \pm 0.18$ kcal mol^{-1} and $\Delta S^\ddagger = -20.4 \pm 0.6$ cal K^{-1} mol^{-1} for the closing of the seven-membered ring. The second-order rate constants for ring opening, k^r_{Cl}, are 3.1 × 10^{-5} M^{-1} s^{-1} for the six-membered ring and (1.04 ± 0.03) × 10^{-4} M^{-1} s^{-1} for the seven-membered ring. This behavior is compared to that of the previously reported 1,2-diaminoethane complex[1] and the analogous bis(monodentate amine) systems and the significance of ring size and amine basicity in determining the reactivity of these systems is examined.

Introduction

In a recent paper[1] we examined the kinetics of the forward and reverse processes of the reaction,

$$cis\text{-}[Pt(dmso)(enH)Cl_2]^+ \rightarrow [Pt(dmso)(en)Cl]^+ + H^+ + Cl^-$$

the purpose of the work being to establish the parameters governing the dimethyl sulfoxide system in order to be able to examine the effect of increasing the size of the chelate ring. A number of other studies involving flexible five-membered chelate rings have been reported, notably those of Carter and Beattie[2] and, more recently, of Natile et al.[3] There are few systematic and relevant kinetic studies of the ring-opening and ring-closing processes with flexible six-membered ring systems and none, to our knowledge, involving a seven-membered ring. In this paper we examine the above reaction with the complexes of 1,3-diaminopropane (tn) and 1,4-diaminobutane (bn).

Experimental Section

***cis*-Dichloro(dimethyl sulfoxide)((3-aminopropyl)ammonium)platinum(II) Chloride.** $[Pt(dmso)(tn)Cl]Cl$ (0.16 g, 0.40 mmol), prepared by the method of Romeo et al.,[4] was dissolved in the minimum amount of methanol and the solution stirred vigorously while concentrated hydrochloric acid (0.20 cm^3, 2 mmol) was added. The mixture was left to stand for 24 h at room temperature and the required product separated out as a white powder. This was filtered off, washed carefully with 2 or 3 drops of concentrated hydrochloric acid to remove a small amount of yellow impurity and then washed with ether, and finally air-dried.

Anal. Calcd for $C_5H_{17}N_2OCl_3PtS$: C, 13.2; H, 3.77; N, 6.16; Cl, 23.4; S, 7.05. Found: C, 13.5; H, 3.90; N, 6.17; Cl, 23.6; S, 7.02.

The infrared spectrum is characterized by a barely resolved strong doublet at 1112 and 1105 cm^{-1}, assigned to ν_{S-O} of S-bonded dimethyl sulfoxide. In the range 500–300 cm^{-1} there are peaks at 447 (m), 378 (m), 348 (s), and 319 (s) cm^{-1}, the latter two being assigned to ν_{Pt-Cl}, the splitting being characteristic of a pair of cis chlorines.

***cis*-Dichloro(dimethyl sulfoxide)((4-aminobutyl)ammonium)platinum(II) chloride** was prepared in a similar way from $[Pt(dmso)(bn)Cl]Cl$[4] but using ethanol as solvent.

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Anal. Calcd for $C_6H_{19}N_2OCl_3PtS$: C, 15.4; H, 4.09; N, 5.98; Cl, 22.7; S, 6.84. Found: C, 15.1; H, 4.11; N, 5.89; Cl, 22.3; S, 6.44.

The infrared spectrum contains a pair of strong peaks at 1119 and 1132 cm^{-1} characteristic of S-bonded dimethyl sulfoxide and very strong peaks at 446, 375, 341, and 319 cm^{-1}, the last two being assigned to ν_{Pt-Cl} of a *cis*-dichloro complex.

Kinetics. The kinetics of the reactions were followed by methods that have already been described.[1] Phosphoric acid–sodium dihydrogen phosphate buffers were used to maintain a constant pH in the range 1.5–2.8 and sodium dihydrogen phosphate–disodium hydrogen phosphate buffers were used in the region 4.8–6.3. The pH was measured with a digital Radiometer PHM 52 pH meter using a glass electrode and a calomel reference electrode with saturated sodium chloride solution as the liquid junction (the potassium salt leads to precipitation problems in the perchlorate media used). The instrument was calibrated with an equimolar H_3PO_4–NaH_2PO_4 buffer solution for work in the acid region. The ionic strength was adjusted with sodium perchlorate.

Results

(a) Kinetics of the Closing of the Six-Membered Ring. As in the case of the 1,2-diaminoethane analogue,[1] the spectrum of an aqueous solution of *cis*-$[Pt(dmso)(tnH)Cl_2]Cl$ changes to that of chelated $[Pt(dmso)(tn)Cl]Cl$ at a rate that depends upon the pH and the chloride concentration of the solution. However, under comparable conditions, the rate is very much slower and it was necessary to carry out the studies at higher pH. Since the reaction releases protons, it was necessary to use buffers to maintain the constant pH and preliminary experiments showed that phosphoric acid–phosphate buffers did not interfere with the reaction. The need to measure the pH with a glass electrode made it necessary to change the salts used to provide the chloride and maintain constant ionic strength from LiCl and $LiClO_4$ to NaCl and $NaClO_4$, since the lithium salts adversely affected the glass electrode. Reactions were carried out at 30.0 °C and constant ionic strength ($\mu = 2.0$; $NaClO_4$) and the total buffer concentration was held constant at 0.10 M. The concentration of the complex was small enough to ensure first-order kinetics in any run and good linear semilogarithmic plots were obtained in all cases. For a constant concentration of chloride, the plot of k_{obsd} (the measured first-order rate constant) against $[H^+]^{-1}$ was linear and (except possibly at highest chloride ion concentration) passed through the origin. The slopes and intercepts of these plots, derived from a linear least-squares analysis of the primary data, are collected in Table I and it will be seen that the rate of reaction is retarded by added chloride. As in the case of the 1,2-diaminoethane complex,[1] a plot of the slope, S, against $[Cl^-]^{-1}$ is curved. The intercept, S_∞ (the value of S when $[Cl^-]^{-1} = 0$), can be precisely determined and the plot of $(S - S_\infty)^{-1}$ against $[Cl^-]$ is linear, with a finite intercept. This is consistent with a relationship of the form, $S = (a[Cl^-] + b)(c + [Cl^-])^{-1}$. Rather than derive the values of a, b, and c by graphical methods, as in the previous paper, we used a nonlinear least-squares curve fitting program and an IBM 113 computer. The calculated values of the slopes are compared with the experimental data in Table I.

Table I. Slopes and Intercepts of the Plots of k_{obsd} against $[H^+]^{-1}$ as a Function of $[Cl^-]$ for the Reaction

$$cis\text{-}[Pt(dmso)(tnH)Cl_2]^+ \rightarrow [Pt(dmso)(tn)Cl]^+ + Cl^- + H^{+\,a-c}$$

$10^2[Cl^-]$/M[d]	range of pH variation	10^6 × slope/$M^{-1}\,s^{-1}$ (exptl)	10^6 × slope/$M^{-1}\,s^{-1}$ (calcd)[e]	10^4 × intercept/s^{-1}
0.113	1.52–2.54	8.83 ± 0.19	8.97	+0.64 ± 0.33
0.163	1.57–2.52	7.30 ± 0.21	7.04	+0.03 ± 0.42
0.213	1.56–2.58	5.94 ± 0.08	5.87	−0.05 ± 0.16
0.313	1.58–2.58	4.46 ± 0.10	4.51	+0.13 ± 0.20
0.413	1.59–2.59	3.53 ± 2.59	3.74	0.00 ± 0.10
0.613	1.57–2.58	2.93 ± 0.06	2.91	−0.25 ± 0.12
0.813	1.59–2.79	2.41 ± 0.13	2.47	0.00 ± 0.43
1.013	1.59–2.78	2.16 ± 0.03	2.19	+0.15 ± 0.10
1.513	1.58–2.77	1.81 ± 0.07	1.81	+0.25 ± 0.25
4.013	1.58–2.73	1.37 ± 0.03	1.32	+0.18 ± 0.10
10.0	2.23–2.75	1.18 ± 0.04	1.13	+0.02 ± 0.15
50.0	1.70–2.75	1.07 ± 0.03	1.04	+0.20 ± 0.08

[a] At 30.0 °C. [b] $\mu = 2.0$ ($NaClO_4$). [c] [Complex] = 1.3 × 10^{-4} M. [d] Initial concentration. [e] Calculated from the relationship slope = $(1.01 \times 10^{-6}[Cl^-] + 1.29 \times 10^{-8})/([Cl^-] + 4.36 \times 10^{-4})$.

Table II. Rate Constants for the Reaction

$$cis\text{-}[Pt(dmso)(bnH)Cl_2]^+ \rightarrow [Pt(dmso)(bn)Cl]^+ + Cl^- + H^{+\,a-d}$$

C_S/C_H[e]	pH	10^{-4} × $[H^+]^{-1}$/M^{-1}	10^4 × k_{obsd}/s^{-1}	10^4 × k_{calcd}/s^{-1} [f]
0.094	4.858	7.21	2.41	2.84
0.14	5.054	11.3	3.70	3.71
0.23	5.308	20.3	5.75	5.63
0.36	5.537	34.4	8.70	8.64
0.60	5.800	63.1	14.8	14.8
0.96	6.033	108	24.9	24.3
1.56	6.263	183	40.0	40.4

[a] In water at 30.0 °C. [b] $\mu = 1.2$ ($NaClO_4$). [c] [Complex] = 1.3 × 10^{-4} M. [d] $[Cl^-]$ = 1.00 M. [e] $C_H = [NaH_2PO_4]$, $C_S = [Na_2HPO_4]$ ($C_H + C_S$ = 0.10 M). [f] Calculated using $k_{obsd} = (2.13 \times 10^{-9})[H^+]^{-1} + 1.30 \times 10^{-4}$.

(b) Kinetics of the Closure of the Seven-Membered Ring. The ring closing reactions of *cis*-$[Pt(dmso)(bnH)Cl_2]Cl$ in water are much slower than those of the corresponding 1,3-diaminopropane and 1,2-diaminoethane complexes and cannot be studied at low pH because of the unfavorable position of equilibrium with respect to ring opening. In the pH region where ring closing was fast enough to be followed conveniently, the solvento complex, *cis*-$[Pt(dmso)(bnH)ClH_2O]^{2+}$, undergoes extensive acid dissociation and is in equilibrium with cis-$[Pt(dmso)(bnH)ClOH]^+$, a species of different reactivity with respect to ring closing. Preliminary experiments showed that, at the lower chloride concentrations, the pH dependence of the observed rate constant was more complicated than a simple $[H^+]^{-1}$ relationship and so, rather than spend a great deal of time analyzing this relationship in order to evaluate the additional parameters, we decided to follow the reaction in the presence of a large enough excess of chloride to ensure that the pathways involving the aquo complex and its hydroxo conjugate base only made a negligible contribution to the rate of reaction.[5] The observed rate constants are collected in Table II. There is a linear relationship between k_{obsd} and $[H^+]^{-1}$ which takes the form, $k_{obsd}/s^{-1} = [(2.13 \pm 0.02) \times 10^{-9})]\cdot[H^+]^{-1} + (1.30 \pm 0.20) \times 10^{-4}$.

The ring-closing reaction was also studied under conditions where the pH was high enough for all the substrate to be in the form of the unprotonated monodentate (ring-opened) species. These reactions, which were too fast to follow in the case of 1,2-diaminoethane and 1,3-diaminopropane, were still fast enough to require the use of a stopped-flow spectrophotometer in the case of 1,4-diaminobutane. The substrate was dissolved in 0.010 M HCl and 1.19 M NaCl and the reaction was started by mixing this with a solution of 0.014 M NaOH and 1.19 M NaCl, the sodium chloride serving to maintain the required ionic strength and ensure that the bulk of the substrate was in the form of the chloro complex. The first-order (pH-independent) rate constants, each of which is the average of three independently determined values, measured at different temperatures, are collected in Table III, together with the derived activation parameters.

(c) Kinetics of Ring Opening. When the chelated species are dissolved in water containing sufficient sodium chloride and acid, they undergo ring-opening substitution reactions and

Table III. Rate Constants for the Reaction

cis-[Pt(dmso)(bn)Cl$_2$] → [Pt(dmso)(bn)Cl]$^+$ + Cl$^-$ [a–c]

temp/°C	20.0	25.0	30.0	35.0	40.0	45.0
k_{obsd}/s^{-1}	12.5	16.1	22.3	28.8	38.3	50.3
k_{calcd}/s^{-1} [d]	12.2	16.5	22.1	29.2	38.3	49.9

[a] In water at 30.0 °C, μ = 1.2 (NaCl). [b] [Complex] = 5 × 10^{-4} M. [c] k_{obsd} measured at 270 nm. [d] Rate constants calculated using $\Delta H^\ddagger = 9.80 \pm 0.18$ kcal mol^{-1} and $\Delta S^\ddagger = -20.4 \pm 0.6$ cal deg^{-1} mol^{-1}.

Table IV. Rate Constants for the Reaction

[Pt(dmso)(diamine)Cl]$^+$ + H$^+$ + Cl$^-$ →
cis-[Pt(dmso)(diamineH)Cl$_2$]$^+$ [a–c]

diamine	[H$^+$]/M	[Cl$^-$]/M	$10^5 k_{obsd}/s^{-1}$
pn	0.40	0.84	3.0[d]
pn	0.40	1.25	4.0[d]
pn	0.40	1.65	5.5[d]
bn	0.0040	0.20	2.3
bn	0.0040	0.40	4.0
bn	0.0040	0.60	5.8
bn	0.0040	0.80	8.1
bn	0.0040	1.00	10.6
bn	0.0040	1.16	12.0

[a] In water at 30.0 °C. [b] μ = 1.2 (NaClO$_4$) except where noted. [c] [Complex] = 1.0 × 10^{-3} M. [d] μ = 2.0 (NaClO$_4$).

the change in spectrum is the reverse of that observed for the ring-closing reactions. The correspondence is exact within experimental error for the 1,4-diaminobutane system, but, with the 1,3-diaminopropane complex, there are discrepancies at wavelengths below 270 nm which are the result of a greater than expected absorbance of the reaction product. The changes are not consistent with a relatively slow subsequent process and, although we have been unable to identify the cause of this disturbance, we believe it to be the result of a small amount of strongly absorbing by-product. The kinetics were determined from the change in absorbance at 280 nm where the spectral changes are completely reversible. Preliminary studies showed that, as in the case of the 1,2-diaminoethane complex,[1] the rate of ring opening was independent of [H$^+$]. The first-order rate constants for the opening of the six- and seven-membered ring species are collected in Table IV. A plot of k_{obsd} against [Cl$^-$] for the 1,4-butanediamine complex is linear with slope = (1.04 ± 0.03) × 10^{-4} M^{-1} s^{-1} and passes through the origin (intercept = (−0.6 ± 2.7) × 10^{-6} s^{-1}). The data for the opening of the six-membered ring are insufficient to merit a least-squares treatment but, if the line is anchored by an intercept corresponding to the rate constant for the forward reaction when [Cl$^-$] ≫ K_{Cl} and [H$^+$] = 0.40 M, i.e., $k = 2.5 \times 10^{-6}$ s^{-1}, the best straight line has a slope = 3.14×10^{-5} M^{-1} s^{-1}.

Discussion

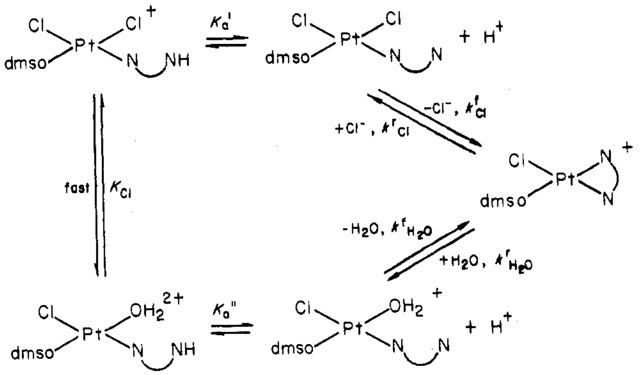
The kinetics of the forward and reverse reactions

$$cis\text{-}[\mathrm{Pt(dmso)(N\text{-}NH)Cl_2}]^+ \rightleftarrows [\mathrm{Pt(dmso)(N\text{-}N)Cl}]^+ + \mathrm{H}^+ + \mathrm{Cl}^-$$

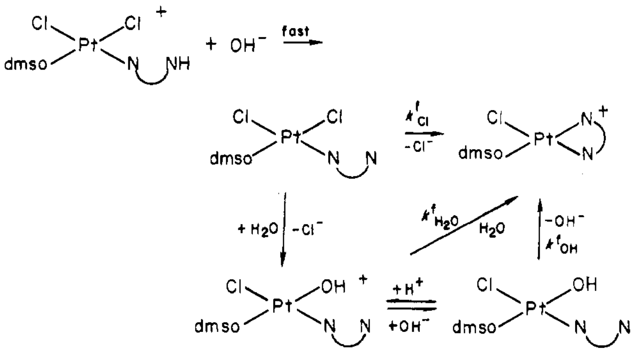
where N-N = 1,3-diaminopropane and 1,4-diaminobutane are fully consistent with the mechanism previously proposed for the 1,2-diaminoethane analogue,[1] in which a rapid and reversible solvolysis of the chloride from the ring-open species led to two parallel paths for ring closure, Scheme I. When equilibrium lies completely to the right, the rate law for ring closing takes the form

$$k_{obsd} = ([\mathrm{Cl}^-] + K_{\mathrm{Cl}})^{-1}\{k^{\mathrm{f}}{}_{\mathrm{Cl}}K_{\mathrm{a}}'[\mathrm{Cl}^-] \times (K_{\mathrm{a}}' + [\mathrm{H}^+])^{-1} + k^{\mathrm{f}}{}_{\mathrm{H_2O}}K_{\mathrm{a}}''K_{\mathrm{Cl}}(K_{\mathrm{a}}'' + [\mathrm{H}^+])^{-1}\}$$

Scheme I



Scheme II



and, since all experiments, apart from those involving the 1,4-diaminobutane complex in alkaline solution, were carried out under conditions where [H$^+$] ≫ $K_a'' \sim K_a'$, this reduces to

$$k_{obsd} = ([\mathrm{Cl}^-] + K_{\mathrm{Cl}})^{-1}(k^{\mathrm{f}}{}_{\mathrm{Cl}}K_{\mathrm{a}}'[\mathrm{Cl}^-] + k^{\mathrm{f}}{}_{\mathrm{H_2O}}K_{\mathrm{a}}''K_{\mathrm{Cl}})[\mathrm{H}^+]^{-1}$$

in the case of the 1,3-diaminopropane complex, where the data were gathered over a wide range of chloride concentrations, and

$$k_{obsd} = k^{\mathrm{f}}{}_{\mathrm{Cl}}K_{\mathrm{a}}'[\mathrm{H}^+]^{-1} + k^{\mathrm{f}}{}_{\mathrm{H_2O}}K_{\mathrm{a}}''K_{\mathrm{Cl}}[\mathrm{Cl}^-]^{-1}[\mathrm{H}^+]^{-1}$$

in the case of the 1,4-diaminobutane complex where data were gathered under conditions where [Cl$^-$]/K_{Cl} = ca. 2 × 10^3. Since $K_a' \sim K_a''$ and $k^f{}_{H_2O}$ is unlikely to be greater than 50 times $k^f{}_{Cl}$, the second term cannot contribute more than a few percent to the magnitude of k_{obsd} and we have therefore simplified the relationship to $k_{obsd} = k^f{}_{Cl}K_a'[H^+]^{-1}$. The experimental rate law has an extra, acid-independent term because the reaction does not go to completion under the experimental conditions. Treated as a reversible first-order process, $k_{obsd} = k^f + k^r$, so that $k_{obsd} = k^f{}_{Cl}K_a'[H^+]^{-1} + k^r$. An independent, and much more precise, determination of k^r starting with the chelated complex (see below) gives $k^r = 1.04 \times 10^{-4}$ s^{-1} under these conditions, which agrees reasonably well with the observed (1.30 ± 0.20) × 10^{-4} s^{-1}.

In the study of the ring closing reaction of the 1,4-diaminobutane complex in alkaline solution, the assumption that the chloro to aquo equilibrium is established much more rapidly than the ring closure is no longer justified and the reaction must be represented by Scheme II. In order to get a simple first-order rate law with no significant induction period in keeping with the experimental observations, there must be no significant accumulation of intermediates, i.e., $k^f{}_{H_2O}$ and $k^f{}_{OH}$ must be very much greater than $k^f{}_1$. Under these circumstances the rate law simplifies to $k_{obsd} = k^f{}_{Cl} + k^f{}_1$. In view of the fact that the aquo complex is a weak acid (pK_a = 5–6), the rate of deprotonation in 0.004 M OH$^-$ will be much faster than ring closure and any material passing through the k^f_1 pathway will be converted to the hydroxo species. Preliminary experiments at low chloride concentration indicate that the hydroxo species must be considerably less labile than the aquo species and the absence of significant quantities in the above experiment can only be explained if $k^f_{Cl} \gg k^f_1$. It is also possible to estimate the value of k^f_1 from a knowledge of the behavior of an analogous monodentate system

$$cis\text{-}[Pt(dmso)(am)Cl_2] + am \rightarrow cis\text{-}[Pt(dmso)(am)_2Cl]^+ + Cl^-$$

This reaction has been studied in aqueous solution for am = cyclohexylamine,[1] where $k^f_1 = 0.15\ s^{-1}$, and it is known that when the cis amine is varied k^f_1 increases as the basicity decreases.[7] However, since the basicity of 1,4-diaminobutane ($pK_a(1) = 10.68$)[8] is much the same as that of cyclohexylamine (10.66),[9] it is unlikely that k^f_1 for the ring-closing reaction is much greater than $0.2\ s^{-1}$ and so this contribution can be neglected. Consequently it is possible to assign the observed value $22.3\ s^{-1}$ at 30.0 °C to k^f_{Cl} for the ring closing of *cis*-[Pt(dmso)(bn)Cl_2]. It is of interest to note that the activation parameters for this reaction, $\Delta H^{\ddagger} = 9.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = 20.4$ cal K^{-1} mol^{-1}, are not particularly unusual for an associative substitution reaction at platinum(II), and the entropy of activation suggests that the reduction in the degrees of freedom on forming the transition state leading to the seven-membered ring does not differ greatly from the reduction that occurs when an independent amine becomes attached in the transition state. The studies of ring closing in buffer solution, where $K_a'' \ll [H^+]$, give a value of $k^f_{Cl}K_a' = (2.13 \pm 0.02) \times 10^{-9}$ M s^{-1} for the 1,4-diaminobutane complex, which, when combined with the independently determined value for k^f_{Cl}, gives $K_a' = 9.55 \times 10^{-11}$ at 30.0 °C ($pK_a' = 10.03$).

The closing of the six-membered ring was studied in more detail but direct determination of k^f_{Cl} was not possible because, under the conditions where $K_a' \gg [H^+]$, the reaction was too fast to follow by stopped-flow techniques. The parameters calculated from the data in Table I can be used to determine some of the rate constants from Scheme I. Thus $a = k^f_{Cl}K' = (1.01 \pm 0.07) \times 10^{-6}$ M s^{-1}, $b = k^f_{H_2O}K_a''K_{Cl} = (1.29 \pm 0.07) \times 10^{-8}$ M^2 s^{-1}, and $c = K_{Cl} = (4.36 \pm 0.84) \times 10^{-4}$ M. In order to separate these constants it is necessary to estimate values for K_a' and K_a''. In the case of the 1,2-diaminoethane complex[1] we assumed that $K_a' = 10^{-8}$ M since it was found that, in the few cases where the pK_a of the free nitrogen of a monodentate 1,2-diaminoethane was known, the basicity was not particularly sensitive to the nature of the "quaternizing" substituent on the other nitrogen. Having now determined the basicity of the free nitrogen of 1,4-diaminobutane when the other nitrogen is coordinated to $-Pt(dmso)Cl_2$ at the same temperature and at a fairly similar ionic strength, we shall attempt to estimate K_a' for monodentate 1,2-diaminoethane and 1,3-diaminopropane by assuming that a relationship of the form, $-\log K_a' = pK_a(amH_2^{2+}) + \alpha$, holds. The pK_a values must all relate to measurements made under identical conditions of temperature and ionic strength for all three amines and α, an arbitrary constant is calculated by using the experimental data for the 1,4-diaminobutane complex. A wide selection of values is available in the literature for the pK_a's of the amines, especially 1,2-diaminoethane,[10] and we have chosen the data of Fernelius et al.[8,11] since these come from the most recent study of all three amines carried out under identical conditions in the same laboratory. Schwartzenbach et al.[12,13] also report basicity data for the three amines, but under different experimental conditions; their data yield an identical value for K_a' of the 1,3-diaminopropane complex but a somewhat larger value for 1,2-diaminoethane (2.3×10^{-8} M). However, more recent measurements of Nasanen[14-18] of the basicity of 1,2-diaminoethane and 1,3-diaminopropane agree almost exactly with those of Fernelius.[8,11] The values of K_a', $K_a'k^f_{Cl}$ and k^f_{Cl} for the formation of the five-, six-, and seven-membered ring species are collected in Table V. The refined value of K_a' for the 1,2-diaminoethane species is some 70% greater than the "order of magnitude" value used in the earlier paper[1] but the arguments presented are in no way affected by the change. However, in view of the approximations used, it will be unwise to draw any inferences from small differences in the derived data.

Table V. Comparison of Ring-Closing and Ring-Opening Rate Constants and Other Information for the Reaction

$$cis\text{-}[Pt(dmso)(N\text{-}NH)Cl_2]^+ \rightleftharpoons [Pt(dmso)(N\text{-}N)Cl]^+ + H^+ + Cl^-$$

	N-N		
	en	tn	bn
ring size	5	6	7
pK_{a_1} [a]	9.98	10.50	10.68
pK_{a_2} [a,b]	6.79	8.33	9.04
pK_a'	7.77[c]	9.31[c]	10.02[d]
$10^6k^f_{Cl}K_a'$/M s^{-1}	1501[e]	1.01[d]	0.00213[d]
k^f_{Cl}/s^{-1}	8830	2060	22.3
k^f_{Cl}(calcd)/M^{-1} s^{-1} [f]	7.0	4.4	3.7
effective molarity/M	1260	468	6.0
$10^4k^r_{Cl}$/M^{-1} s^{-1}	1.0[e]	0.31[d]	1.04[d]
$10^4k^r_{Cl}$(calcd)/M^{-1} s^{-1} [g]	640	25	5.7
calcd/found	640	81	5.5
$K_{rc} = k^f_{Cl}/k^r_{Cl}$/M^{-1}	8.8×10^7	6.6×10^7	2.1×10^5

[a] From ref 8. [b] From ref 11. [c] See text. [d] This work. [e] From ref 1. [f] See text. [g] Using pK_a'.

The first observation that can be made on the data in Table V is that, although, under similar conditions of pH and temperature, the 1,2-diaminoethane complex undergoes ring closing much more rapidly than the 1,3-diaminopropane complex, this effect is almost entirely due to the difference in the basicities of the uncoordinated nitrogens and, once this has been taken into account, the rate constants for the closing of the ring differ by a factor of only 4. On the other hand, the 1,4-diaminobutane system is far less reactive and, even after accounting for any basicity difference, the rate constant for the formation of the seven-membered ring is some 10^2 times smaller than those for the closing of the five- and six-membered ring. It is instructive to estimate the rate constants, k^f_{Cl}, for the analogous reactions of the monodentate amines, i.e.

$$cis\text{-}[Pt(dmso)(am)Cl_2] + am \rightarrow cis\text{-}[Pt(dmso)(am)_2Cl]^+ + Cl^-$$

when the monodentate amine, am, has the same basicity as the chelating diamine in order to see (a) how much the variation in the basicity of the diamine can account for the observed reactivity differences and (b) how the act of forming a ring affects the reactivity. In a study of the above reaction in methanol[7] it was found that the rate constant was insensitive to the basicity of the entering amine but was influenced by the basicity of the amine cis to the leaving group in accordance with the linear free energy relationship, $\log k^f_{Cl} = -0.39pK_a(amH^+) + \beta$. Assuming that the change in solvent from methanol to water only affected the magnitude of β, and using the experimentally determined value for am = cyclohexylamine in water,[1] the values of k^f_{Cl}(calcd) shown in Table V were obtained.[19] It is clear that the basicity differences cannot account for the difference between the reaction of the 1,4-diaminobutane complex and the others. In order to relate the calculated second-order rate constants [k^f_{Cl}(calcd)] to the experimental first-order rate constants for ring closing, it is useful to introduce the concept of the "effective molarity" of the free and of the chelate molecule, as being the ratio of k^f_{Cl}:k^f_{Cl}(calcd).[21] The revised value for the five-membered ring, 1200 M, is less than that estimated previously (4000 M) using an order of magnitude assessment of K_a' but is closer to the value of 800 M estimated by Carter and Beattie for the chloroethylenediamine system.[2] Natile et al.[3] find a higher effective molarity (ca. 4000 M) in the ring-closing reactions of bidentate bis(2-aminoethyl)methylamine- and tris(2-aminoethyl)aminedichloroplatinum(II) but in all of these cases no correction was made for the differing cis effects in the experimental and reference reactions. There is very little comparative information about the closing of six-membered rings. Mønsted and Bjerrum[22] report that the rate constant for ring closing in *trans*-$[Pt(NH_3)(NH_2CH_2CH_2CH_2NH_3)Cl_2]^+$ is some 10^2 times slower than that for the analogous 1,2-diaminoethane complex but are unable to correct for the difference in the basicity of the two amines, which could easily account for the difference in reactivity. Volshtein et al.[23] have compared the rates of ring closing of N-bonded α- and β-amino acids and find that the five-membered ring is formed only 2–3 times faster than the six-membered ring. Indeed, as the solvent is changed from pure water to ethanol–water mixtures, the difference between the rates of closure diminishes as the water content decreases. In reactions of this sort the carboxylate is unprotonated and no correction is needed for differences in basicity. Unfortunately there are no data for the second-order rate constants for entry of monodentate carboxylates in systems of this sort and so it is not possible to estimate an effective molarity. The value of 600 M for the effective molarity of the free end of 1,3-diaminopropane is still far too large to have physical significance and suggests that, as in the case of the 1,2-diaminoethane complex, the average ground-state conformation of the deprotonated open-chain complex resembles the monodentate system some of the way along its reaction coordinate. It is not suggested that any bonding has developed between the free nitrogen and the platinum (i.e., incipient five-coordination) but simply that solvent reorganization is well under way. The small difference between the effective molarities of the free end of the Pt–N–C–C–N and Pt–N–C–C–C–N species is to be noted and it will be of interest to see whether this is usual for Pt(II) by examining other systems.

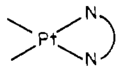
The effective molarity of the 1,4-diaminobutane complex, 6 M, is well below the maximum that can be achieved by restricting the free end of the ligand to sites in close proximity to the platinum and suggests that there are many allowed conformations where the amine nitrogen is well away from the metal. The enhanced reactivity of the uncoordinated end of the amine with respect to ring closing is sufficiently small to allow intermolecular bridging to compete with intramolecular ring closure at high complex concentration and it is relevant to note that, under preparative conditions, $[Pt(dmso)Cl_2NH_2(CH_2)_4NH_2Pt(dmso)Cl_2]$ is an important reaction product.[4] Recently, Illuminati et al.[24] have reviewed a number of ring closing reactions involving nucleophilic attack at carbon in which very large rings are formed and indicate that, in many such systems, the effective molarity tends toward a limiting value between 10^{-1} and 10^{-2} M and becomes independent of ring size with 12- or more membered rings. The closure of seven-membered rings at carbon with alkoxy or phenoxy type nucleophiles is accompanied by effective molarities of 30–100 M and the difference between the closure of five- and six-membered rings is very much more marked than it is for reaction at platinum. It is therefore important to examine the closure of much larger rings at platinum in order to see whether there is any parallel between the reactions of platinum and carbon and also to see how much of the chelate effect remains with larger-than-seven-membered rings.

The rate law for the reverse (ring opening) reaction, also shown in Scheme I, will take the form $k_{obsd} = k^r_{H_2O} + k^r_{Cl}[Cl^-]$ when the reaction is carried out under pseudo-first-order conditions with a low enough pH and sufficient chloride present to prevent significant reversibility of the ring-opening process. These conditions were achieved with the 1,4-diaminobutane complex, and the absence of an intercept in the plot of k_{obsd} vs. $[Cl^-]$ indicates that $k^r_{H_2O}$ makes a negligible contribution to the reaction rate and can be ignored. With the 1,3-diaminopropane complex it was not possible to achieve conditions where ring opening went to completion and where the chloride-independent term could be measured precisely. Treating the reaction as a reversible first-order process, i.e., $k_{obsd} = k^r + k^f$, where $k^f = k^f_{Cl}K_a'[H^+]^{-1}$, it was found that $(k_{obsd} - k^f)[Cl^-]^{-1}$ was reasonably constant so that, in this case also, the contribution from the chloride-independent $k^r_{H_2O}$ pathway was negligible. Under the experimental conditions, $k^f = 2.5 \times 10^{-6}\ s^{-1}$, so that, even under the least favorable circumstances, the ring-opening process should go 90% toward completion. The values of k^r_{Cl} are collected in Table V, together with the previously reported value for the 1,2-diaminoethane complex.

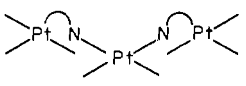
Bearing in mind the crudeness of the data for the opening of the five-membered ring, it is remarkable how similar are the rate constants for the opening of the three rings in spite of the considerable differences in the pK_{a2} values of the three diamines. The question therefore arises as to whether this similarity is the result of a coincidental cancelling of two opposing effects or whether it has a more significant meaning. As in the case of the ring-closing reactions, the analogous monodentate bis(amine) system has been studied in methanol solution.[7] For the reaction

$$cis\text{-}[Pt(dmso)(am)_2Cl]^+ + H^+ + Cl^- \rightarrow cis\text{-}[Pt(dmso)(am)Cl_2] + amH^+$$

$\log k^r_{Cl} = -0.91pK_a(amH^+) + \gamma$, so that, by assuming that the gradient did not change when the solvent was changed from methanol to water and determining γ from the known rate constant for the reaction with am = cyclohexylamine,[1] it should be possible, in principle, to estimate the rate constant for displacing an amine of the same basicity as the chelate but without its bidenticity. Unfortunately, it is not possible to measure the basicity of a chelating amine when it is chelated. In the discussion for the ring opening of the 1,2-diaminoethane complex[1] we used the estimated pK_a' value for monodentate en in order to calculate a value for the rate constant for ring opening and the revised value for this, together with the similarly calculated values for the other two complexes, are shown in Table V as k^r_{Cl}(calcd). In all three cases, the calculated rate constant is larger than that determined experimentally. For the opening of the five-membered ring the observed value is some 600 times less than that calculated, this ratio drops to 81 for the six-membered ring and then down to 6 for the seven-membered ring. We now have serious doubts as to whether this is a valid model. The use of the pK_a' value as a measure of the effective basicity of a chelating diamine in order to assess cis effects and leaving group effects is based on the assumption that



is equivalent to

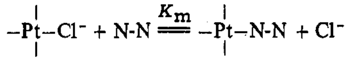


which implies that the whole of the influence of the coordination of one nitrogen upon the properties of the other is passed inductively along the chain or carbon atoms. However, we are not dealing with two separate substituents since both nitrogens are attached to the same platinum and it is eminently reasonable to suggest that the dominant influence involves the interactions of the two nitrogens and the platinum, the length of the carbon chain serving only to modify the ligand "bite" and the orientation of the amine protons. As a consequence the effective basicity of the nitrogens in these chelating diamines should remain roughly constant and the rate constants for ring opening should not differ greatly from one complex to another. This is what we found for the three $NH_2(CH_2)_nNH_2$ complexes examined and so we conclude that this similarity is more than the coincidental cancelling of opposing effects. However, it will be necessary to examine many more compounds before one can decide whether or not this is a general phenomenon.[25]

The equilibrium constants for the ring-closing process can be calculated using the relationship $K_{rc} = k^f_{Cl}/k^r_{Cl}$, and these are also listed in Table V. It will be seen that, while the stability constant does decrease on increasing the ring size, the change from a five-membered to a six-membered ring only leads to a small decrease in stability. In general, the directly measured stability constants for labile systems show a greater destabilization than this. For example, log K_1 for the complexes of Cd(II) with diamines of the type $NH_2(CH_2)_nNH_2$ changes from 5.3 ($n = 2$)[8] to 4.6 ($n = 3$)[26] to 3.6 ($n = 4$)[27] (although the last value is measured at a lower temperature than the others). For Ni(II), log K_1 changes from 7.52 to 6.40 on going from $n = 2$ to $n = 3$,[8] while for Cu(II) the change is from 10.67 to 9.72.[8] With sulfur donors the ring size effect seems to be even greater. Cattalini[28] has shown that, in the equilibrium

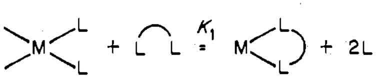
$$Pd(S\text{-}S)I_2 + 2I^- = PdI_4^{2-} + S\text{-}S$$

(S-S = $RS(CH_2)_nSR$), the five-membered ring species are some 10^2 to 10^3 times more stable than their six-membered ring analogues, although the ratio decreases quite significantly as the donor power of the ligand decreases. Strictly speaking, it is necessary to combine the equilibrium constant for ring closing with that for the addition of the chelate in the monodentate form, i.e.,



$$-Pt-Cl^- + N\text{-}N \xrightleftharpoons{K_m} -Pt-N\text{-}N + Cl^-$$

in order to make a valid comparison, i.e., for



$K_1 = K_mK_{rc}$. However, although the monodentate equilibrium has not yet been studied experimentally, it seems unlikely that the variation of K_m on changing the length of the carbon chain will be of a sufficient magnitude or even in the right direction to make the difference of K_1 much greater than that of K_{rc} for the five- and six-membered ring species. The lower basicity of the donor atom in monodentate 1,2-diaminoethane is likely to make k^r_{Cl} for the monodentate reaction larger than that for the analogous 1,3-diaminopropane species. On the other hand, we know that the rate constant for the reaction between $[Pt(Me_2S)Cl_3]^-$ and 1,2-diaminoethane is some four times greater than expected[29] but do not know whether or not the other diamines have a similar enhanced nucleophilicity. For this reason we have now commenced a study of the reactions of diamines of various length with $[Pt(dmso)Cl_3]^-$ and $[Pt(Me_2S)Cl_3]^-$ and the results will be reported in due course.

Registry No. *cis*-[Pt(dmso)(tnH)Cl$_2$]Cl, 66842-52-2; *cis*-[Pt(dmso)(bnH)Cl$_2$]Cl, 66842-53-3; [Pt(dmso)(tn)Cl]Cl, 62120-27-8; [Pt(dmso)(bn)Cl]Cl, 62120-28-9.

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