Kinetic Studies on Closure of a Second Condensed Ring in [Bis(2-aminoethyl)methylamine hydrochloride]dichloro- and Dichloro[tris(2-aminoethyl)amine bis(hydrochloride)]-platinum(II) Complexes

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The title complexes [PtCl$_2$(bama·HCl)] and [PtCl$_2$(taa·2HCl)] with the tri- and quadri-dentate ligands acting as bidentate have been prepared and the kinetics of closure of the second condensed ring have been studied in aqueous solution. From stopped-flow measurements in basic media at 25 °C, the rate constants for the reactions [PtCl$_2$(bama)] $\longrightarrow$ [PtCl(bama)]$^+$ + Cl$^-$ and [PtCl$_2$(taa)] $\longrightarrow$ [PtCl(taa)]$^+$ + Cl$^-$ are $k_1 = 2.1 \pm 0.1$ and $k_1'' = 4.3 \pm 0.2$ s^{-1}. This implies that only a probability factor of two can satisfactorily account for the difference in the observed rates. Kinetic measurements at pH < 7 have shown that under these conditions the reactive species are unprotonated [PtCl$_2$(bama)] and monoprotonated [PtCl$_2$(taa·HCl)]; the ring-closure process is faster for the tris(2-aminoethyl)amine (taa) complex than for the bis(2-aminoethyl)methylamine (bama) complex, and anchimeric assistance of the protonated end of taa on entry of the unprotonated end (by ion pairing with the leaving chloride) is proposed.

THERE have been several studies on ring closure in octahedral complexes,[1-4] but only few papers concerning the analogous reactions in square-planar substrates.[5,6] In the latter complexes, since the activation process is

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[1] A. Kowalak, K. Kustin, R. F. Pasternack, and S. Petrucci, *J. Amer. Chem. Soc.*, 1967, **89**, 3126.

[2] W. B. Makinen, A. F. Pearlmutter, and J. E. Stuehr, *J. Amer. Chem. Soc.*, 1969, **91**, 4083.

[3] A. G. Sykes and R. N. F. Thorneley, *J. Chem. Soc.* (*A*), 1969,

[4] J. P. Jones and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 470.

[5] S. P. Tanner, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1967, **6**, 1089.

[6] M. J. Carter and J. K. Beattie, *Inorg. Chem.*, 1970, **9**, 1233.

primarily associative, the effect of chelation on the rate of substitution is expected to be much more dramatic than in octahedral substrates in which the activation process is essentially dissociative. Moreover, when the closing of a second condensed ring is involved the chelate effect is generally assumed to be smaller, and in several monosubstitution reactions in square-planar complexes, containing a polydentate ligand, equilibria between tri- and bi-dentate species have been suggested.[7-11]

We have prepared the *cis*-dichloro[tris(2-aminoethyl)-amine bis(hydrochloride)]platinum(II), $[PtCl_2(taa{\cdot}2HCl)]$, and *cis*-[bis(2-aminoethyl)methylamine hydrochloride]-dichloroplatinum(II), $[PtCl_2(bama{\cdot}HCl)]$, complexes and studied the rate of ring closure of the second condensed ring in both acidic and basic solutions. The results can be compared with the rates of substitution by unidentate ammonia [12] and half-bonded ethylenediamine [6] in analogous aminechloro-complexes of Pt^{II}. By comparing the kinetic behaviour of the tri- and quadri-dentate ligands it should be possible to see if the fourth nitrogen of taa (which cannot co-ordinate to platinum) has some influence on the rate of ring closure.

EXPERIMENTAL

The salt $K_2[PtCl_4]$ was purchased from Johnson, Matthey and Co.; tris(2-aminoethyl)amine (taa), sodium perchlorate, perchloric acid, acetic acid, sodium acetate, sodium nitrate, and sodium hydroxide were all reagent-grade products. Bis(2-aminoethyl)methylamine (bama) was prepared according to the reported procedure.[13]

Preparations.—*[Bis(2-aminoethyl)methylamine hydrochloride]dichloroplatinum*(II), $[PtCl_2(bama{\cdot}HCl)]$. Following the procedure of Watt and Cude,[14] $K_2[PtCl_4]$ (15 g, 0.036 mol) and bama·3HCl (16.3 g, 0.072 mol) were dissolved in water (300 cm^3) and kept at 70 °C for 10 d (at higher temperatures extensive decomposition to metallic platinum occurred). The resulting yellow solution was concentrated to 40—50 cm^3 and cooled to room temperature; white KCl precipitated at this stage. On further concentration (20—30 cm^3) and cooling the desired product separated out, and was recrystallized from 1N hydrochloric acid (10 cm^3), yield >70%, m.p. 253 °C (decomp.) {Found: C, 14.3; H, 4.0; Cl, 25.8; N, 9.9. $[PtCl_2(bama{\cdot}HCl)]$ requires C, 14.3; H, 3.8; Cl, 25.4; N, 10.0%}.

Bis[bis(2-aminoethyl)methylamine]chloroplatinum(II) *tetrachloroplatinate*(II), $[PtCl(bama)]_2[PtCl_4]$. This complex was prepared using the same experimental conditions of the previous preparation but adopting a shorter reaction time (3—4 d). The resulting orange solution was concentrated to 60 cm^3 and cooled to room temperature. Dark red crystals separated out, were washed with cold water, and dried *in vacuo* over P_4O_{10}, yield >50%, m.p. 273 °C (decomp.) {Found: C, 11.7; H, 2.9; Cl, 20.9; N, 8.1. $[PtCl(bama)]_2[PtCl_4]$ requires C, 11.6; H, 2.9; Cl, 20.6; N, 8.1%}.

[Bis(2-aminoethyl)methylamine]chloroplatinum(II) *perchlorate*, $[PtCl(bama)][ClO_4]$. This complex was prepared from $[PtCl(bama)]_2[PtCl_4]$ by anion exchange using a column of Dowex 1×4 (50—100 mesh) resin, m.p. 261 °C (decomp.) {Found: C, 13.7; H, 3.6; Cl, 16.2; N, 9.5. $[PtCl(bama)][ClO_4]$ requires C, 13.4; H, 3.4; Cl, 15.9; N, 9.4%}.

Dichloro[tris(2-aminoethyl)amine bis(hydrochloride)]platinum(II), $[PtCl_2(taa{\cdot}2HCl)]$. This complex was prepared by two different methods. (*i*) A solution of $K_2[PtCl_4]$ (16.6 g, 0.04 mol) and taa·3HCl (20.44 g, 0.08 mol) in water (300 cm^3) was allowed to react for 15 d at 70 °C until the colour of the solution, initially dark red, became yellow. The solution was filtered, concentrated to 50 cm^3, and cooled to room temperature whereupon white crystals of KCl separated out. By further concentration of the solution, crystals of $[PtCl_2(taa{\cdot}2HCl)]$ were obtained. These were recrystallized from 1N HCl, yield >70%, m.p. 188 °C (decomp.) {Found: C, 14.1; H, 4.2; Cl, 29.0; N, 11.0. $[PtCl_2(taa{\cdot}2HCl)]$ requires C, 14.8; H, 4.1; Cl, 29.2; N, 11.5%}. (*ii*) The salt $K_2[PtCl_4]$ (16.6 g, 0.04 mol) was treated with twice the stoicheiometric amount of taa·3HCl (20.44 g, 0.08 mol) partly neutralized by addition of NaOH (0.12 mol). A fast reaction took place with the separation of a reddish solid (which was insoluble in the more common solvents and analysed as $[Pt_2Cl_4(taa)]$). The reaction mixture was then adjusted to pH 0 with HCl and kept at 70 °C for 8 d. The solid gradually dissolved and the colour of the solution turned yellow. From this solution $[PtCl_2(taa{\cdot}2HCl)]$ was isolated as in (*i*).

Chloro[tris(2-aminomethyl)amine hydroperchlorate]platinum(II) *perchlorate*, $[PtCl(taa{\cdot}HClO_4)][ClO_4]$. The complex $[PtCl_2(taa{\cdot}2HCl)]$ (2.4 g, 0.005 mol) was dissolved in a few millilitres of water and treated with the stoicheiometric amount of lithium hydroxide (0.005 mol). Perchloric acid (0.01 mol) and excess of $Li[ClO_4]$ were then added and white crystals of the desired product separated out, yield >70%, m.p. 225 °C (decomp.) (Found: C, 12.3; H, 3.4; Cl, 18.2; N, 9.6. $[PtCl(taa{\cdot}HClO_4)][ClO_4]$ requires C, 12.5; H, 3.3; Cl, 18.4; N, 9.7%}.

I.r. Spectra.—The i.r. spectrum of the complex $[PtCl_2(bama{\cdot}HCl)]$ showed absorptions characteristic of protonated amine groups and two platinum–chlorine stretches at 324 and 295 cm^{-1}. The complex $[PtCl(bama)][ClO_4]$ showed only one Pt–Cl stretching vibration at 338 cm^{-1} and no bands characteristic of quaternary amine groups. The i.r. spectrum of $[PtCl_2(taa{\cdot}2HCl)]$ showed two Pt–Cl stretching frequencies at 331 and 318 cm^{-1}; $[PtCl(taa{\cdot}HClO_4)][ClO_4]$ had only one Pt–Cl stretching at 337 cm^{-1}.

Acid–Base Titrations.—The complex $[PtCl_2(bama{\cdot}HCl)]$ behaved as a monobasic acid and could be titrated with sodium hydroxide. Unfortunately the intermediate species (II) (see Scheme below), which represents the free base in the protic dissociation equilibrium, undergoes chelation reaction to give (III) and therefore it was not possible to measure K_a from the titration; complex (II) was continuously removed from the equilibrium by the reaction (II) $\longrightarrow$ (III), and after the addition of each aliquot portion of titrant the pH varied with time and its value was always lower than expected. The complex $[PtCl_2(taa{\cdot}2HCl)]$ behaved as a dibasic acid and could be titrated with sodium hydroxide. The value of the first dissociation constant could not be measured for the same reason as above. However, after the addition of the first

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[7] C. E. Wieck and F. Basolo, *Inorg. Chem.*, 1966, **5**, 576.

[8] A. J. Poë and D. H. Vaughan, *Inorg. Chim. Acta*, 1967, **1**, 255.

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

[10] D. L. Fant and C. F. Weick, *Inorg. Chem.*, 1973, **12**, 1864.

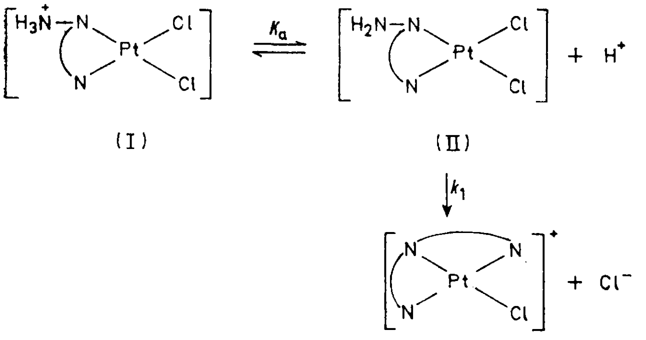
[11] K. A. Johnson, J. C. Lim, and J. L. Burmeister, *Inorg. Chem.*, 1973, **12**, 124.

[12] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Amer. Chem. Soc.*, 1965, **87**, 241.

[13] F. G. Mann, *J. Chem. Soc.*, 1934, 466.

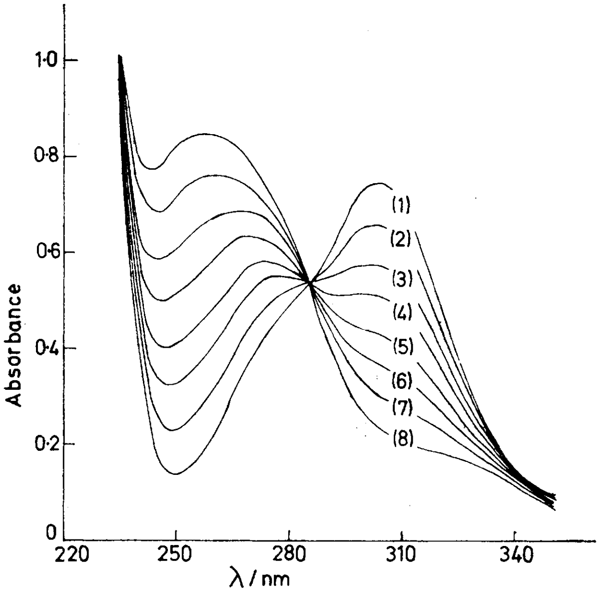
[14] G. W. Watt and W. A. Cude, *Inorg. Chem.*, 1968, **7**, 335.

equivalent of base the original complex transforms to [PtCl(taa·HCl)]Cl which could be titrated with base; the constant of its dissociation equilibrium {$[PtCl(Htaa)]Cl_2 \rightleftharpoons [PtCl(taa)]^+ + H^+ + 2Cl^-$} was calculated from the titration as (1.6 ± 0.2) × 10^{-8} mol dm^{-3}. This value is very similar to that obtained kinetically for the acid dissociation of $[PtCl(en)(en·HCl)]^+$ (en = ethylenediamine).[6]



(I) (II) (III)

Kinetics.—Rate data in acidic solutions were obtained either spectrophotometrically using an Optica CF4R double-beam instrument or titrimetrically using a Radiometer pH-stat recording titrator. In the former case, separate aqueous solutions of 0.4 mol dm^{-3} acetic acid containing the reacting complex and of 0.4 mol dm^{-3} sodium acetate were brought to the reaction temperature and then mixed so as to attain the required pH and placed in the thermostatted cell of the spectrophotometer. The kinetics were followed by observing absorption changes in the u.v. region of the spectrum. Preliminary experiments showed that all absorbing species obeyed Beer's law in the solvent used, and the appearance from the start of a well defined isosbestic point indicated that single-stage processes were occurring (Figure). First-order rate constants were calculated from plots of $\ln(A_\infty - A_t)$ against time, where A_t and A_∞ are the absorbances at time t and after at least six half-lives respectively. The experimentally determined rate constants $k_{obs.}$ (s^{-1}) are summarized in Tables 1 and 2.



Spectroscopic course of the reaction $[PtCl_2(bama·HCl)] \longrightarrow [PtCl(bama)]Cl + HCl$. $[PtCl_2(bama·HCl)] = 3.6 \times 10^{-3}$, $[H^+] = 2.4 \times 10^{-5}$, $I = 0.4$ mol dm^{-3} at 25 °C. Curves (1)—(8) show, respectively, spectra at zero time and after 10, 21, 32, 50, 70, 100, and 200 min

TABLE 1

First-order rate constants for the reaction $[PtCl_2(bama·HCl)] \longrightarrow [PtCl(bama)]Cl + HCl$, at various hydrogen-ion concentrations and temperatures and $I = 0.4$ mol dm^{-3}

θ_c/°C	$10^6[H^+]$/mol dm^{-3}	$10^4k_{obs.}/s^{-1}$
19.5	1.31	20.40
	2.77	9.95
	10.65	2.95
	24.84	1.38
24.5	1.25	41.90
	2.64	22.21
	10.18	6.36
	23.72	3.22
	55.30	1.54
31.5	2.50	52.70
	9.63	14.51
	22.45	7.05
	52.33	3.40
40.0	5.17	76.10
	13.80	31.00
	31.00	16.20
	82.50	7.56
24.5 *	2.68	20.30
	8.47	7.33
	21.18	2.87
	26.77	2.26
	42.37	1.44
	63.73	1.04

* The rate constants were not measured spectrophotometrically but titrimetrically with a pH-stat.

TABLE 2

First-order rate constants for the reaction $[PtCl_2(taa·2HCl)] \longrightarrow [PtCl_2(taa·HCl)]Cl + HCl$ at various hydrogen-ion concentrations and temperatures and $I = 0.4$ mol dm^{-3}

θ_c/°C	$10^6[H^+]$/mol dm^{-3}	$10^3k_{obs.}/s^{-1}$
19.5	2.77	6.47
	4.39	4.14
	10.65	1.99
	24.84	0.97
	57.91	0.49
25.0	2.64	14.01
	5.94	6.17
	10.18	3.96
	15.82	2.62
	23.72	1.83
	35.57	1.34
	55.30	0.95
	94.75	0.66
	213.0	0.48
	265.3	0.34
	449.3	0.18
34.0	5.42	24.85
	9.28	14.76
	21.64	7.08
	50.44	4.04
	86.42	2.42
40.0	8.86	32.40
	13.78	20.93
	20.66	15.27
	48.17	7.77
	82.50	5.17
	185.5	2.67

The reaction rates in acidic solution at 25 °C were also obtained using a pH-stat titrator and measuring the rate at which base was added to maintain a constant pH. In a typical experiment, 3 × 10^{-5} mol of complex was dissolved in 5 cm^3 of an aqueous solution containing 10^{-3} mol dm^{-3} $HClO_4$ and 0.4 mol dm^{-3} K[NO_3] and placed in the thermostatted vessel of the titrator. The pH value was then selected and the rate of addition of base (0.1 mol dm^{-3} NaOH) was measured. The initial addition of base required to bring the pH to the selected value was not taken into account. The rate constant was obtained from a semilogarithmic plot of the difference between the total amount of base required and that added at time *t* against time.

The rates of reaction in basic solutions were obtained spectrophotometrically with a Durrum D-110 stopped-flow instrument by rapid mixing of a solution of the reactant substrate dissolved in 0.4 mol dm^{-3} Na[ClO_4] containing 0.001 mol dm^{-3} $HClO_4$ with a second solution of 0.4 mol dm^{-3} Na[ClO_4] containing sufficient NaOH to bring the resulting solution to pH$>$11. The observed rate constants were calculated from conventional plots of $\ln(A_\infty - A_t)$ against time. The data are collected in Table 4.

RESULTS

Reaction of [$PtCl_2$(bama·HCl)].—The complex [$PtCl_2$(bama·HCl)] is stable in acidic solution at pH <3, but at lower acidity a reaction takes place. The spectroscopic course of this reaction is shown in the Figure; a well defined isosbestic point was observed at 285 nm and the final spectrum corresponded to that of a sample of [PtCl(bama)][ClO_4] prepared independently. During the course of reaction HCl was released, and by using a pH-stat titrator it was possible to measure the rate and the stoicheiometry of the reaction by measuring the rate at which base was consumed and the total amount which was required. The kinetics were followed either spectrophotometrically or titrimetrically, a constant ionic strength of 0.4 mol dm^{-3} and an initial complex concentration of 3 × 10^{-3} mol dm^{-3} being used in all cases. The observed rate constants are given in Table 1.

The rate of reaction was pH dependent and $k_{obs.}$ was a linear function of the reciprocal of the hydrogen-ion concentration in accord with expression (1), where B_0 is the

$$k_{obs.} = B_0 + (B_1/[H^+]) \qquad (1)$$

intercept at $[H^+]^{-1} = 0$ and B_1 is the gradient of a plot of $k_{obs.}$ against $[H^+]^{-1}$. The values of these constants at different temperatures, calculated by least-squares methods, are given in Table 3. The agreement between the rate constants measured spectrophotometrically and with a pH-stat is satisfactory and the observed discrepancies can be ascribed to the different measuring techniques.

The rate of the reaction in basic solution was obtained spectrophotometrically by rapid mixing of a solution of [$PtCl_2$(bama·HCl)] dissolved in 0.4 mol dm^{-3} Na[ClO_4] and containing 0.001 mol dm^{-3} $HClO_4$ with a second solution of 0.4 mol dm^{-3} Na[ClO_4] containing sufficient NaOH to bring the mixed solution to pH >11. The observed rate constant at 25 °C was 2.1 ± 0.1 s^{-1}.

Reaction of [$PtCl_2$(taa·2HCl)].—The kinetic behaviour of the complex [$PtCl_2$(taa·2HCl)] was completely analogous to that above. The observed rate constants are given in Table 2. In acidic media $k_{obs.}$ was a linear function of $[H^+]^{-1}$ and the intercepts at $[H^+]^{-1} = 0$, B_0, and the gradients, B_1, of the linear plots of $k_{obs.}$ against $[H^+]^{-1}$ at various temperatures, obtained by least-squares calculations, are given in Table 3. At pH >10, the rate was independent of pH, and from stopped-flow experiments a value of 4.2 ± 0.2 s^{-1} was obtained at 25 °C.

TABLE 3

Values of the parameters B_0 and B_1 obtained by least-squares calculations from plots of $k_{obs.}$ against $1/[H^+]$, and the enthalpy and entropy of activation obtained from B_1 data using an unweighted least-squares program (The error in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ was derived from the standard deviations of B_1 using the formula for indirect errors.)

Substrate	θ_c/°C	10^9B_1/ mol dm^{-3} s^{-1}	10^4B_0/s^{-1}
[$PtCl_2$(bama·HCl)]	19.5	2.62 ± 0.06	0.4 ± 0.3
	24.5	5.17 ± 0.46	1.2 ± 1.8
	31.5	12.9 ± 0.3	1.1 ± 0.6
	40.0	37.5 ± 1.7	3.6 ± 1.8
[$PtCl_2$(taa·2HCl)]	19.5	17.1 ± 0.8	2.7 ± 1.7
	25.0	36.2 ± 0.6	2.6 ± 0.9
	34.0	128.0 ± 6.0	11.7 ± 5.7
	40.0	271.1 ± 14.0	17.5 ± 8.2

	$\Delta H^\ddagger$/kcal mol^{-1}	$\Delta S^\ddagger$/cal K^{-1} mol^{-1}
[$PtCl_2$(bama·HCl)]	23.0 ± 0.5	−19 ± 2
[$PtCl_2$(taa·2HCl)]	24.0 ± 0.6	−12 ± 2

TABLE 4

Parameters at 25 °C and $I = 0.4$ mol dm^{-3}

$k_1 = 2.1 \pm 0.1$ s^{-1}
$k_1'' = 4.3 \pm 0.2$ s^{-1}
$K_a = (2.5 \pm 0.3) \times 10^{-9}$ mol dm^{-3}
$K^{a} = (1.6 \pm 0.2) \times 10^{-8}$ mol dm^{-3}
$K^{b} = (1.8 \pm 0.3) \times 10^{-10}$ mol dm^{-3}

[a] Equilibrium constant for acid dissociation of the complex [PtCl(taa·$HClO_4$)][ClO_4]. [b] Second and third dissociation constants of bama·3HCl.

DISCUSSION

The B_0 term refers to an acid-independent mechanism analogous to that found in the ring closing of the [PtCl(en)(en·HCl)]$^+$ substrate and which was explained in terms of a solvent path.[6] In our case the contribution of this path to the total rate was negligible and will not be discussed any further. The observed rate is therefore almost totally composed of the pH-dependent term which refers to a path in which only the unprotonated free end of the ligand can co-ordinate to platinum. In the suggested mechanism for the [$PtCl_2$(bama·HCl)] complex the ring-closure step is preceded by a rapid acid–base equilibrium [equations (2) and (3)]. The derived

$$[PtCl_2(bama{\cdot}HCl)] \overset{K_a}{\rightleftharpoons} [PtCl_2(bama)] + HCl \qquad (2)$$

$$[PtCl_2(bama)] \xrightarrow{k_1} [PtCl(bama)]^+ + Cl^- \qquad (3)$$

expression for the rate constant is given in equation (4).

$$k_{obs.} = \frac{K_a k_1}{K_a + [H^+]} \qquad (4)$$

The [$PtCl_2$(taa·2HCl)] complex can behave as a dibasic acid, and therefore we have two intermediate species [$PtCl_2$(taa·HCl)] and [$PtCl_2$(taa)] which can give the chelation reaction. The resulting mechanism is expressed by equations (5)—(8) from which (9) can be deduced for the rate constant.

Both expressions (4) and (9) reproduce the observed rate law assuming that in acidic media K_a, K_a', and

K_a'' are much smaller than $[H^+]$. In basic media, pH 11, we have $[H^+] \ll K_a$, K_a', and K_a'' and the reaction

$$[PtCl_2(taa{\cdot}2HCl)] \overset{K_a'}{\rightleftharpoons} [PtCl_2(taa{\cdot}HCl)] + HCl \quad (5)$$

$$[PtCl_2(taa{\cdot}HCl)] \overset{K_a''}{\rightleftharpoons} [PtCl_2(taa)] + HCl \quad (6)$$

$$[PtCl_2(taa{\cdot}HCl)] \xrightarrow{k_1'} [PtCl(taa{\cdot}HCl)]^+ + Cl^- \quad (7)$$

$$[PtCl_2(taa)] \xrightarrow{k_1''} [PtCl(taa)]^+ + Cl^- \quad (8)$$

$$k_{obs.} = \frac{K_a'K_a''k_1'' + K_a'k_1'[H^+]}{K_a'K_a'' + K_a'[H^+] + [H^+]^2} \quad (9)$$

rate is no longer dependent on the acid-dissociation constants and the values of k_1 and k_1'' are directly measured. The ring-closure rate constants for the $[PtCl_2(bama)]$ complex were 2.1 ± 0.1 s^{-1} at 25 °C, and from the value of B_1 at the same temperature K_a could be calculated as $(2.5 \pm 0.3) \times 10^{-9}$ mol dm^{-3}. The value of k_1'' found for the $[PtCl_2(taa)]$ complex was 4.3 ± 0.2 s^{-1}, but, since there is no relation of any kind between k_1'' and k_1', the acid-dissociation constant K_a' cannot be deduced from the value of B_1'.

The value of K_a can be compared with the second and third dissociation constants of bama·3HCl which refer to deprotonation of primary amine groups; these have the same value of $(1.8 \pm 0.3) \times 10^{-10}$ mol dm^{-3}, and thus the terminal amine group is a weaker base in co-ordinated bama than it is in the free ligand. This behaviour is not unexpected since when two adjacent amine groups are protonated the first ionization constant is always higher than the second [15] and co-ordination of a tertiary amine group to the metal is somewhat similar to a protonation. For the equilibria (10) and (11), the constants 1.2×10^{-8} and 1.1×10^{-8} mol dm^{-3} were obtained [6] which are intermediate between the first and second ionization constants of en·2HCl (en′ = unidentate

$$[PtCl_2(en{\cdot}HCl)_2] \rightleftharpoons [PtCl_2(en{\cdot}HCl)(en')] + HCl \quad (10)$$

$$[PtCl(en)(en{\cdot}HCl)]^+ \rightleftharpoons [PtCl(en)(en')]^+ + HCl \quad (11)$$

ethylenediamine). For equilibrium (12) we measured a dissociation constant of $(1.6 \pm 0.2) \times 10^{-8}$ mol dm^{-3} which is very similar to that of equilibrium (11). This is expected since the two complexes have the same charge and the same donor atoms.

$$[PtCl(taa{\cdot}HCl)]^+ \rightleftharpoons [PtCl(taa)]^+ + HCl \quad (12)$$

It is to be noted that the value of k_1'' is twice that of k_1. Both constants refer to ring closure of the totally unprotonated species and the difference can be explained on the basis of a statistical factor of two. In fact, whereas the taa complex has two equivalent amine groups both available for co-ordination, the other complex has only one. Both values are in the same range of those found by Carter and Beattie [6] for the closing of unidentate en. A full comparison is not possible because of the difference in the group *trans* to the leaving chloride and of the charge of the reacting substrate; however, the rate of closing of the first chelate ring does not seem to differ significantly from the closing of the second condensed ring.

The results in basic media can be compared with the rate of substitution by ammonia obtained from the related platinum(II) complex $[PtCl_2(en)]$ [equation (13)].[12]

$$[PtCl_2(en)] + NH_3 \longrightarrow [PtCl(NH_3)(en)]^+ + Cl^- \quad (13)$$

In the latter case the rate constant was 5×10^{-4} dm^3 mol^{-1} s^{-1} at 35 °C; at the same temperature we found the values of 4.3 ± 0.2 and 8.6 ± 0.3 s^{-1} respectively for k_1 and k_1''. The ring closure is a first-order unimolecular reaction, whereas substitution by ammonia is a second-order bimolecular process. To make a proper comparison one must convert the first-order rate constant (s^{-1}) into a second-order rate constant (dm^3 mol^{-1} s^{-1}) by estimating the effective concentration of the free end of the entering ligand. Assuming that the free end fills a hemisphere of minimum radius 3 Å, Carter and Beattie calculated an effective concentration of 30 mol dm^{-3}.[6] This value is not sufficient to account for the faster rate of ring closure. Apart from the factor of concentration which results in a higher probability of collision of the free end of the ligand with the central metal, other more specific factors, which can influence the effectiveness of collisions, are probably important in the ring-closure processes. The organic chain attached to the free end of the ligand keeps the donor atom at a distance from the co-ordination site which will not vary significantly after co-ordination to the metal; moreover, the direction in which the free end can approach the metal ion is that appropriate for the substitution reaction.

In contrast with what has been found in a basic medium (where the ring-closure rate of taa was twice that of bama), in an acidic medium the closure rate of the quadridentate ligand was about seven times higher than that of the tridentate ligand. Under the latter conditions, the rates are dependent on the products $K_a'k_1'$ and K_ak_1 for taa and bama respectively. The higher value of $K_a'k_1'$ may be due either to a higher acid-dissociation constant ($K_a' > K_a$) or to a higher rate of the ring-closure step ($k_1' > k_1$). From the comparison of the activation parameters of the two systems (Table 3) it appears that, while the difference in $\Delta H^\ddagger$ favours the bama complex by a factor of *ca.* 5, the difference in $\Delta S^\ddagger$ favours the taa complex by a factor of *ca.* 34, the net result being a ratio $K_a'k_1' : K_ak_1$ of *ca.* 7. If we assume that the higher rate of chelation of the taa complex is mainly due to $k_1' > k_1$, this can be explained by assuming that in the taa complex there is anchimeric assistance of the protonated amine on entry of the unprotonated amine. An interaction between the protonated group and the leaving chloride would result in partial charge neutralization with consequent

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[15] 'Stability Constants of Metal–Ion Complexes,' eds. L. G. Sillén and A. E. Martell, Special Publ., No. 17, The Chemical Society, London, 1964.

reduced solvation and larger activation entropy,[16] as is actually found. The activation enthalpy would not be greatly affected since the loss in solvation energy could be partly balanced by ion-pair formation.

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[16] F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' 2nd edn., John Wiley, New York, 1967; C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1966; M. L. Tobe, 'Inorganic Reaction Mechanisms,' Nelson, London, 1972.