Chelate Ring Size and Effect of N-Substituents as Limiting Factors for the Formation of Cationic Chloro-diamine-η^2-ethene-platinum(II) Complexes

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The nature of the diamine plays a very critical role in stabilizing the cationic species [Pt(η^2-C_2H_4)Cl(diamine)]$^+$ containing a highly reactive olefin. Hence while N,N,N′,N′-tetramethyl-1,2-diaminoethane (tmen) gave a species isolatable in a pure form, N,N,N′,N′-tetramethyl-1,3-diaminopropane (tmpn) and unsubstituted 1,2-diaminoethane (en) were unable to act as bidentate and gave, as isolatable species, only complexes of the type cis-*[Pt(η^2-C_2H_4)Cl_2(Hdiamine)]$^+$ in which the diamine is protonated and acts as monodentate towards platinum. These results are explained in terms of greater conformational stability of* five- versus six-*membered chelate rings and of* gem-dimethyl substituted *towards* unsubstituted *ring systems (Thorpe–Ingold effect).*

Introduction

We recently reported a cationic platinum complex, [Pt(η^2-C_2H_4)Cl(tmen)]$^+$ (tmen = N,N,N′,N′-tetramethyl-1,2-diaminoethane), which was characterized by having a remarkable thermal stability (its perchlorate decomposed at *ca.* 170 °C) and a high reactivity of the bonded ethene towards nucleophilic agents including amines, NCO^-, N_3^-, NO_2^-, *etc.* [1–6].

Pursuing our studies in this field we found that the diamine plays a very critical role in stabilizing such a cationic species. In this paper we wish to describe the effects of the chelate-ring size and of the alkyl substituents at the aminic nitrogens.

Results and Discussion

The [Pt(η^2-C_2H_4)Cl(tmen)](ClO_4), (**3a**), complex is generated by protolysis, with dilute perchloric acid, of the diplatina species [{Pt(C_2H_4)Cl(tmen)}$_2$(tmen)](ClO_4)$_2$, (**1a**) [2, 7]. This latter is the major product (yield above 90%) in the reaction of Zeise's salt with tmen (1:2 molar ratio) performed in methanol at 0 °C. In order to investigate the effects of chelate-ring size and of N-methyl substituents we performed analogous reactions with N,N,N′,N′-tetramethyl-1,3-diaminopropane (tmpn) and with unsubstituted 1,2-diaminoethane (en). As in the case of tmen, Zeise's salt reacted with tmpn (1:2 molar ratio, in methanol at 10 °C) to give the diplatina complex [{Pt(C_2H_4)Cl(tmpn)}$_2$(tmpn)](ClO_4)$_2$, (**1b**), in quantitative yield. A different behaviour was exhibited by en which in strictly analogous conditions (1:2 molar ratio, in methanol at 0 °C) afforded the triplatina species [{Pt(C_2H_4)Cl(en)}$_3$(en$^-$)](Cl, ClO_4), (**2c**) (en$^-$ = en deprived of a N-bonded proton) in which one end of en is bound to three platinum–ethanide groups and the other is protonated (Table I).

Either (**1b**) or (**2c**) would, in principle, be able to afford the cationic complexes [Pt(η^2-C_2H_4)Cl(tmpn)](ClO_4), (**3b**), and [Pt(η^2-C_2H_4)Cl(en)](ClO_4), (**3c**), respectively by reaction with dilute perchloric acid. This, however, was not the case.

The protolysis reaction of diplatina complex (**1a**) was carried out by treating the substrate with a methanolic solution of $HClO_4$ (three times the stoichiometric amount). While (**1a**) slowly dissolved, the cationic species (**3a**) precipitated out of the solution, both species being sparingly soluble in this solvent. Under strictly analogous conditions either the diplatina complex (**1b**) or the triplatina species (**2c**) gave a clear solution from which any attempt to isolate solid species was unsuccessful, resulting always in decomposition to platinum metal.

Compounds (**1b**) and (**2c**) were therefore submitted to protolysis reaction in 1 mol dm^{-3} HCl. Both dissolved giving a solution [compound (**2c**) gave

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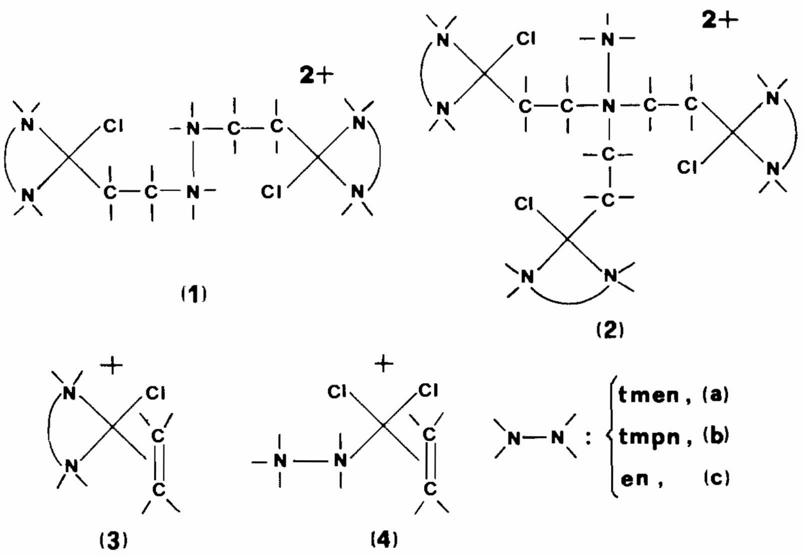


Scheme

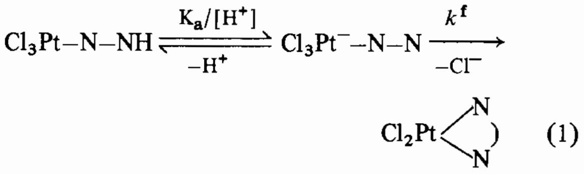
also a small precipitate of [$PtCl_2$(en)]] from which, by concentrating to small volume and cooling to 0 °C, pale yellow crystals of *cis*-[$Pt(\eta^2$-$C_2H_4)Cl_2$(Htmpn)](ClO_4), (**4b**), and *cis*-[$Pt(\eta^2$-$C_2H_4)Cl_2$(Hen)](ClO_4), (**4c**), were obtained (Htmpn and Hen stand for monoprotonated tmpn and en respectively). The same products precipitated directly out of the solution upon bubbling gaseous HCl through a chloroform solution of (**1b**) and (**2c**) respectively (this latter again gave a certain amount of [$PtCl_2$(en)]).

At this stage one obvious procedure for attempting the preparation of (**3b**) and (**3c**) would have been to carry out a ring-closing process in a neutral or weakly basic medium. However under these conditions the reaction ended up always with the formation of neutral species not containing ethene ([$PtCl_2$(tmpn)] and [$PtCl_2$(en)] respectively).

From these data it appears that tmpn and en are only able to give η^2-ethene complexes containing open-hand $Htmpn^+$ and Hen^+ ligands singly bonded to platinum, (**4b**) and (**4c**). On the contrary, under analogous conditions the tmen ligand gave the cationic complex (**3a**) in which the diamine was acting as bidentate towards the metal.

The different behaviour of the three amines can be explained in terms of different chelating ability. In the case of tmen the cationic complex (**3a**) could be formed because the *trans*-labilizing effect of η^2-ethene onto the opposite Pt–N linkage [8] was balanced by the strong tendency of tmen to close the five-membered ring [9]. A non-equivalence of the two Pt–N bonds was clearly shown by the X-ray structure of this complex in which the aminic nitrogen *trans* to the olefin was 0.08 Å farther apart from the metal than the other nitrogen *trans* to chlorine [1]. Apparently the bond-weakening caused by the *trans* ethene is such that neither in the case of tmpn nor in the case of en can compound (**3**) be isolated.

Therefore it appears that the different behaviour of tmen and tmpn resides in the higher stability of five- *versus* six-membered chelate rings. We had found previously that the species of composition [$Pt(\eta^2$-$C_2H_4)Cl_2$(diamine)] had in solution a pure five-coordinate geometry (both ends of the diamine co-ordinated to platinum) only in the case of tmen; in the case of tmpn the co-ordination was five only at −35 °C while at room temperature there was fluxionality between four- and five-coordinate geometries. Furthermore, in the case of tmbn (tmbn = N,N,N′,N′-tetramethyl-1,4-diaminobutane) the co-ordination geometry of the complex was definitely four although both ends of the diamine were made equivalent in the n.m.r. time scale by a fast head-to-tail rearrangement of the ligand [10]. The different tendency to ring formation between tmen and tmpn was also evident from kinetic studies of ring closing in [$PtCl_3$(Htmen)] and [$PtCl_3$(Htmpn)] complexes [eqn. (1)] where the rate constant k^f was higher by a factor



$$Cl_3Pt\text{–N–NH} \underset{-H^+}{\overset{K_a/[H^+]}{\rightleftharpoons}} Cl_3Pt^-\text{–N–N} \xrightarrow[-Cl^-]{k^f} Cl_2Pt\langle\overset{N}{\underset{N}{)}} \qquad (1)$$

of *ca.* 200 in the former than in the latter case [11].

The non-isolation of (**3**) in the case of en, where the greater stability of the five-membered ring should be preserved, must be understood in terms of effect of substituents at the N-atoms of the diamine. It is well established, both in organic and organometallic

TABLE I. Selected Analytical, I.r., and N.m.r. Data.

Compound	Diamine[a]	Elemental analysis[b]				I.r.[c]		^1H n.m.r.[d] δ (η^2-C_2H_4)
		C	H	Cl	N	ν(Pt–C_2H_4)	ν(Pt–Cl)	
[{Pt(C_2H_4)Cl(diamine)}$_2$(diamine)](ClO_4)$_2$	tmen (1a)	24.7 (24.8)	5.6 (5.3)	13.3 (13.3)	7.7 (7.9)	500	325	
	tmpn (1b)	27.1 (27.1)	5.5 (5.6)	12.7 (12.8)	7.5 (7.6)	500	315 br	
[{Pt(C_2H_4)Cl(diamine)}$_3$(diamine$^-$)](Cl, ClO_4)[e]	en (2c)	14.4 (14.6)	4.0 (3.8)	15.4 (15.4)	9.5 (9.7)	510	320	
[Pt(η^2-C_2H_4)Cl(diamine)](ClO_4)	tmen (3a)	20.2 (20.2)	4.3 (4.2)	15.0 (15.0)	5.9 (5.9)	458	340	4.79(61)
[Pt(η^2-C_2H_4)Cl_2(Hdiamine)](ClO_4)[f]	tmen (4a)	18.9 (18.8)	4.1 (4.1)	21.2 (20.8)	5.5 (5.5)	485 390	350 322	
	tmpn (4b)	20.3 (20.7)	4.4 (4.1)	20.4 (20.3)	5.1 (5.4)	490 395	335 325 sh	4.54(66)
	en (4c)	10.2 (10.6)	2.6 (2.9)	23.8 (23.4)	5.9 (6.2)	470 390[g]	340 325	4.51(65)

[a] Tmen = N,N,N′,N′-tetramethyl-1,2-diaminoethane, tmpn = N,N,N′,N′-tetramethyl-1,3-diaminopropane, en = 1,2-diaminoethane. [b] %, calculated values in parentheses. [c] Values in cm^{-1}. [d] Values in p.p.m. downfield from TMS, J(Pt–H) in parentheses, solvent deuteromethanol. [e] Diamine$^-$ = diamine deprived of a N-bonded proton. [f] Hdiamine = monoprotonated diamine. [g] Tentative assignment.

chemistry, that cyclization reactions are favoured by the presence of certain substituents on the ring-forming atoms. It also appears that this effect is most relevant if two methyl groups are attached to the same carbon or nitrogen atom, and for this reason it has been called 'gem-dimethyl effect' or also 'Thorpe–Ingold effect' after its discoverers [12, 13]. Therefore in the case of en, as compared with tmen, the tendency to close the five-membered ring is expected to be smaller and this could be the reason why the corresponding compound (3) was not formed. Also in this case from kinetic studies of ring closing in four-coordinate platinum(II) substrates, the relative rate of chelate-ring formation in tmen and en was estimated to be *ca.* 100 times bigger in the former than in the latter case.

In conclusion, both the greater conformational stability of five-membered rings and the effect of gem-dimethyl substituents on the ring-forming atoms are required in order to stabilize compound (3). If one of the two requisites is not satisfied, as in the cases of tmpn and en, because of the strong *trans*-labilizing effect of the olefin, only the open-hand species in which the diamine acts as monodentate towards platinum are formed. The co-ordination site *trans* to the olefin is either taken by a chloride ion (as in the case of reaction with 1 mol dm^{-3} aqueous HCl) giving rise to the formation of (4), or, in the absence of other donor groups (as in the case of reaction with dilute perchloric acid), by a solvent molecule which starts a decomposition process ending up with the formation of platinum metal.

Experimental

Starting Materials

1,2-Diaminoethane (en), N,N,N′,N′-tetramethyl-1,2-diaminoethane (tmen), and N,N,N′,N′-tetramethyl-1,3-diaminopropane (tmpn) were commercially available and were purified before use by distillation from potassium hydroxide. Zeise's salt was prepared from $K_2[PtCl_4]$ and ethene according to [14]. All other chemicals were commercial reagent-grade products and were used without further purification.

Preparations and Reactions

$[\{Pt(C_2H_4)Cl(L)\}_2(L)](ClO_4)_2$, (L) = tmen, (1a), and tmpn, (1b). An excess of diamine (2 mmol) was added under stirring to a solution of Zeise's salt (1 mmol) in methanol containing a three-fold excess of $Li[ClO_4]$ and kept at 0 °C. The reaction mixture was allowed to warm until 10 °C and stirred for 2 h while the yellow precipitate initially formed dissolved and a white product separated out; this was collected on a sintered-glass filter, washed with methanol and water, and dried (yield 90% referred to platinum).

$[\{Pt(C_2H_4)Cl(en)\}_3(en^-)](Cl, ClO_4)$, (2c)

This compound was prepared as above by adding 2 mmol of en to a methanolic solution of 1 mmol Zeise's salt containing a three-fold excess of $Li[ClO_4]$ and kept at 0 °C. Also in this case a yellow precipitate formed first but it turned quickly to off-white before the addition of amine was complete. This was collected, washed with methanol and water, and dried (yield 80% referred to platinum).

Reaction with Dilute Perchloric Acid

Thrice the stoichiometric amount of acid was added to a suspension of the substrates (0.2 g) in methanol (5 cm^3). In the case of compound **(1a)** while the starting material dissolved a new product, **(3a)**, precipitated out of the solution [2]. In the case of compounds **(1b)** and **(2c)** the starting material dissolved in methanol giving a solution which, on concentration under vacuum, afforded an oily product. This was an intractable material and readily reduced to platinum metal on further attempts to crystallize it.

Reaction with 1 mol dm^{-3} Hydrochloric Acid

The acid (5 cm^3) was added to a solid sample (0.2 g) of the complex [**(1a)**, **(1b)**, or **(2c)**] with stirring. In the case of **(1a)** a fast reaction took place with precipitation of $[PtCl_2(tmen)]$ in quantitative yield. In the case of **(1b)** the starting substrate dissolved giving a clear solution. This was concentrated to small volume and cooled to 0 °C affording pale-yellow crystals of **(4b)** which were collected and dried. In the case of **(2c)** contact with 1 mol dm^{-3} HCl caused the initial formation of a yellow precipitate of $[PtCl_2(en)]$ in less than 20% yield arising from platinum–carbon bond cleavage. The filtered solution upon concentration and cooling afforded a pale-yellow solid **(4c)** which was collected and dried.

It is to be noted that compound **(4a)** could not be prepared by this procedure but required the use of concentrated hydrochloric acid [15].

Apparatus

The i.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer as KBr pellets for 4000–400 and as polythene pellets for 400–250 cm^{-1} range. The ^{1}H n.m.r. spectra were obtained with a Varian EM 390 spectrometer using deutero-methanol as solvent and tetramethylsilane as internal standard.

Selected analytical, i.r., and n.m.r. data are given in Table I.

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