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Acidolysis of Diamino Complexes of Platinum(II) with η-Ethene: Preparation of some new Complexes containing Mono-quaternized Ditertiary Amines

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The acidolysis of five-co-ordinate [$Pt(C_2H_4)Cl_2(Me_4en)$], (I), *and four-co-ordinate* [$Pt(C_2H_4)Cl(Me_4en)$](ClO_4), (II), *(Me₄en = N,N,N',N'-tetramethylethylenediamine), is controlled by the* trans *effect of the olefin. Compound* (I) *reacts with HCl to give first ring opening of the chelate diamine and formation of a species with monoprotonated singly-bonded diamine opposite to the unsaturated ligand, then displacement of the second end of the diamine with formation of Zeise's anion. Under analogous conditions compound* (II) *forms* cis-[$Pt(C_2H_4)Cl_2(Me_4enH)$]$^+$, (III), *which reacts further with HCl to give displacement of ethene and formation of the zwitterion* [$PtCl_3(Me_4enH)$], (IV). *This reaction sequence allows through the isolation of ideal substrates to study ringclosing processes. Spectroscopic data for the new complexes containing the mono-quaternized* Me_4enH^+ *ligand are reported and discussed.*

Introduction

In the past years there have been quite a number of studies concerning complexes of transition elements containing cationic ligands, generally bi- or tridentate nitrogen or phosphorus donors in which one of the functional groups had been quaternized, or else olefins containing a quaternized amine function. In some cases the purpose of the work was focussed on the complexing ability of these molecules since the quaternization of one ligating atom would greatly influence the basicity of the second one provided it was not farther than γ position [1–8]. In other cases the interest for preparing such complexes was in the possibility of obtaining suitable substrates for kinetic studies of ring-closure reactions (in this case the quaternization was obtained *via* protonation) which would allow either a quantitative measure of the kinetic chelate effect, or a determination of the chelate ring-size effect [9–12]. We now wish to report on some new platinum(II) complexes containing a mono-quaternized tetramethylethylenediamine ligand.

Experimental

Preparations

[$Pt(C_2H_4)Cl_2(Me_4en)$], (*I*), and [$Pt(C_2H_4)Cl(Me_4en)$](ClO_4), (*II*), (Me_4en = N,N,N',N'-tetramethylethylenediamine) were prepared as previously described [13, 14].

[$Pt(C_2H_4)Cl_2(Me_4enH)$](ClO_4), (III), (Me_4enH = *monoprotonated* Me_4en)

This complex was prepared dissolving [$Pt(C_2H_4)Cl(Me_4en)$](ClO_4) (0.2 g) in concentrated hydrochloric acid (5 cm^3) at room temperature; a yellow solution immediately formed. Quick evaporation of the solvent under vacuum afforded yellow plates of (*III*). The compound is almost insoluble in most organic solvents, it dissolves, however, in acidic water. Found: C, 18.90; H, 4.15; Cl, 21.21; N, 5.52. Calc. for (*III*): C, 18.81; H, 4.14; Cl, 20.82; N, 5.48%.

[$PtCl_3(Me_4enH)$], (IV)

This complex was prepared, as above, dissolving [$Pt(C_2H_4)Cl(Me_4en)$](ClO_4) in concentrated hydrochloric acid; this time, however, the solution was left standing at room temperature for several days while it became deep orange; then, by slow concentration in a dessiccator, it yielded large crystals of compound (*IV*) which were washed with methanol and air dried. The compound is almost insoluble in most organic solvents and barely soluble in water. Found: C, 17.09; H, 4.35; Cl, 25.65; N, 6.58. Calc. for (*IV*): C, 17.21; H, 4.09; Cl, 25.41; N, 6.69%.

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[$Pt(C_2H_4)Cl_2(Me_4pnAg^+)$] ($ClO_4^-$), (V), ($Me_4pn$ = N,N,N',N'-tetramethylpropane-1,3-diamine)

This compound was prepared adding the five-co-ordinate [$Pt(C_2H_4)Cl_2(Me_4pn)$] complex, prepared as already described [13], to a stirred methanolic solution containing a two fold excess of $AgClO_4$. A brown precipitate immediately formed, this was separated by filtration of the mother liquor, washed with methanol, and air dried. Found: C, 16.87; H, 3.56; Cl, 16.55; N, 4.24. Calc. for (*V*): C, 17.10; H, 3.51; Cl, 16.84; N, 4.43%. I.r. spectra in the range 4000–300 cm^{-1} were measured as KBr pellets or nujol mulls on a Perkin-Elmer 457 spectrophotometer and in the range 500–180 cm^{-1} as polythene pellets on a Perkin-Elmer 180 instrument.

Results and Discussion

The cationic η-ethene complex [$Pt(C_2H_4)Cl(Me_4en)$](ClO_4), (*II*), which we recently reported, dissolves readily in concentrated aqueous HCl to give a yellow solution, quick evaporation of the solvent under vacuum leaves a yellow solid, (*III*), the composition of which indicates that a HCl molecule has added to the original compound. Inspection of the i.r. spectrum which shows two intense peaks at 350 and 322 cm^{-1} assignable to ν(Pt–Cl) (the splitting being characteristic of *cis* chlorines having different *trans* substituents), two medium absorption at 485 and 390 cm^{-1} readily assignable to $\nu(Pt{-}C_2H_4)$ and a rather broad band at about 3150 cm^{-1} due to ν(N–H), allows us to formulate (*III*) as *cis*-[$Pt(\eta\text{-}C_2H_4)Cl_2(Me_4enH)$]($ClO_4$).

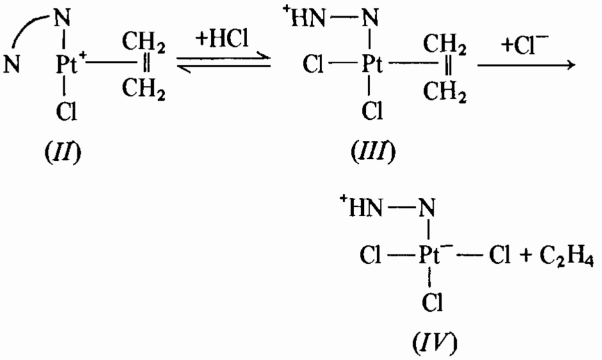
When the hydrochloric solution of (*III*) is allowed to stand a few days at room temperature, it darkens becoming orange red, crystallization yields large crystals of the same colour, which, from analytical data (see experimental) and i.r. spectrum showing protonated and still co-ordinated Me_4en and a multiple ν(Pt–Cl) absorption band centered at 325 cm^{-1} can be formulated as the zwitterion [$PtCl_3(Me_4enH)$], (*IV*).

The absorption bands relative to the monoprotonated co-ordinated diamine in the two complexes are quite different. In the 800–900 cm^{-1} region (where absorptions due to ρCH_2, ρCH_3, and $\nu(C{-}N)_{sym}$ are expected) compound (*III*) has two bands at 875 and 790 cm^{-1} which seem to correspond to a *trans* configuration of the molecule [14], on the contrary compound (*IV*) has a more complex spectrum with bands at 885, 835, and 790 cm^{-1}, accompanied by a rather low ν(N–H) stretching at 3020 cm^{-1}, which seem to indicate a certain amount of hydrogen bonding between the protonated free end of the diamine and chlorine atoms probably within the same molecule.

Differently from halide salts of protonated tertiary amines in which ν(N–H) gives rise to broad absorption bands in the 2700–2350 cm^{-1} region [15], both (*III*) and (*IV*) have ν(N–H) in its normal range.

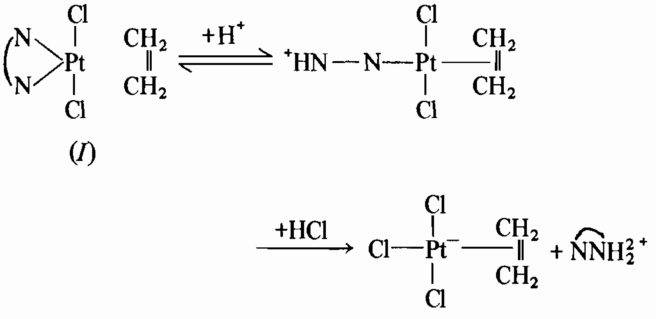
The ready formation of compound (*III*) starting from (*II*) is undoubtedly due to the *trans* influence exerted by the ethene molecule on the opposite nitrogen atom (in the crystal structure of (*II*) the Pt–N distance *trans* to the olefin was significantly longer (2.132 Å) than the Pt–N bond *trans* to chlorine (2.006 Å)) [16].

The residual platinum–amine linkage which is *cis* to ethylene has proved to be very strong and further action of HCl on compound (*III*) leads to olefin substitution and formation of compound (*IV*). Therefore the following reaction sequence can be drawn:



(*II*) (*III*) (*IV*)

In contrast, if we decompose in acidic medium the five-co-ordinate complex [$Pt(C_2H_4)Cl_2(Me_4en)$], (*I*), (from which compound (*II*) is obtained by spontaneous dissociation of a chlorine ion) no formation of compound (*II*) or (*III*) is observed, but the reaction products are Zeise's anion and bis-protonated Me_4en. The possible pathway for the latter reaction is the following:



(*I*)

According to the above scheme monoprotonation of the co-ordinated Me_4en leads to the formation of a square-planar complex having the olefin *trans* to the residual Pt–N bond; this linkage is then weakened and the diamine is easily displaced by chlorine ion. The opening of the chelate ring in compound (*I*) as the first reaction step is supported by the behaviour of analogous complexes with other diamines. For example in the case of the Me_4pn analogue $[Pt(C_2H_4)Cl_2(Me_4pn)]$ (Me_4pn = N,N,N′,N′-tetramethylpropane-1,3-diamine), the species containing bidentate (five-co-ordinate) and monodentate (four-co-ordinate) diamine were in equilibrium with a high conversion rate, in absence of any added acid [13]; moreover if $AgClO_4$ is added to a methanol solution of $[Pt(C_2H_4)Cl_2(Me_4pn)]$ the compound $[Pt(C_2H_4)Cl_2(Me_4enAg^+)](ClO_4^-)$ precipitates out of the solution in quantitative yield.

Both (*III*) and (*IV*), at higher pH, undergo ring-closing processes with the formation of (*II*) and square-planar $[PtCl_2(Me_4en)]$, respectively. Compound (*II*), in turn, reacts with further Cl^- to give again the square-planar $[PtCl_2(Me_4en)]$ complex. Therefore these complexes are ideal substrates for investigating ring-closing reactions, and studies are in progress in this area.

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