Effect of Chain Length of Aliphatic Diamines on the Structure and Reactivity of Dichloro(diamine)(η-ethylene)platinum(II) Complexes

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Bidentate aliphatic diamines react with Zeise's salt, or its dimer, to give complexes of formula [Pt(C_2H_4)Cl_2L] [L = *NNN'N'*-tetramethyl-ethylenediamine (Me_4en), -propane-1,3-diamine (Me_4pn), or -butane-1,4-diamine (Me_4bn)]. In chloroform solution the Me_4en complex has a five-co-ordinate structure up to the temperature (10 °C) where decomposition with release of ethylene readily occurs. The Me_4pn complex (34 °C) exhibits a geometry which is intermediate between four- and five-co-ordination. On decreasing the temperature, the five-co-ordination becomes increasingly important and is attained at −30 °C. The Me_4bn complex at 34 °C has a purely four-co-ordinate structure involving equivalent ends of the diamine (obtained by rapid head-to-tail rearrangement). On decreasing the temperature to −30 °C the four-co-ordinate η-ethylene species is still present but in equilibrium with a new species, probably formed by nucleophilic attack on ethylene of a free end of the diamine. Decomposition studies in 1,2-dichloroethane have shown that the tendency of the [Pt(C_2H_4)Cl_2L] species to release ethylene, giving [PtCl_2L], increases with increasing preference for five- relative to four-co-ordination.

In previous papers [1-3] we reported the preparation of five-co-ordinate π-ethylene complexes of platinum(II) with bidentate *N*-donor ligands containing the α-di-imine unit (L = Z–N=C–C=N–Z; Z = R or NR^1R^2). Closely related to the nitrogen atoms of an imine are those of the hydrotris(pyrazol-1-yl)borate anion which has been shown to stabilize five-co-ordinate platinum(II) complexes with acetylenes, activated olefins,[4-6] and more recently ethylene.[7]

We report here a comparative study of the products obtained by interaction of Zeise's salt (or its dimer) with *NNN'N'*-tetramethyl-ethylenediamine (Me_4en), -propane-1,3-diamine (Me_4pn), and -butane-1,4-diamine (Me_4bn); these ligands can potentially form chelate rings of increasing size.

EXPERIMENTAL

Starting Materials.—The diamines were commercial products, purified before use by distillation from potassium hydroxide. Zeise's salt was prepared according to the method of Cramer *et al.*[8] from potassium tetrachloroplatinate(II) and ethylene gas. Zeise's dimer was prepared from Zeise's salt by the method of Chatt and Searle.[9]

Preparation of Complexes.—[Pt(C_2H_4)Cl_2(Me_4en)] (1). This complex was prepared from stoicheiometric amounts of ligand and Zeise's dimer (1 mmol of Me_4en per 0.5 mmol of [{Pt(C_2H_4)Cl_2}$_2$] in 4—5 cm^3 of methanol at −15 °C). A yellow complex precipitated immediately; it was collected on a sintered glass filter provided with a cooling jacket, washed once with cold methanol, and dried under vacuum. The yield was 50%. The complex was readily soluble in chloroform and acetone, and quite soluble also in methanol, precluding a higher yield [Found: C, 23.1; H, 4.9; Cl, 17.1; N, 6.9. Calc. for (1): C, 23.4; H, 4.9; Cl, 17.3; N, 6.8%].

[Pt(C_2H_4)Cl_2(Me_4pn)] (2). This complex was prepared in a similar way. In this case the final product was much more thermally stable and its solubility in methanol was much lower than that of the previous complex. Therefore the mixing of reactants {1 mmol of Me_4pn and 1 mmol of K[Pt(C_2H_4)Cl_3]} was carried out at 0 °C, and Zeise's salt was employed as starting material with a larger volume of methanol (10—15 cm^3) to avoid coprecipitation of KCl. The yield was 80% [Found: C, 24.6; H, 5.2; Cl, 16.4; N, 6.4. Calc. for (2): C, 25.5; H, 5.2; Cl, 16.7; N, 6.6%].

[Pt(C_2H_4)Cl_2(Me_4bn)]. Two different forms, (3a) and (3b), were obtained. The former was prepared either in methanol, following the procedure previously described for the preparation of (2), or in chloroform adding the stoicheiometric amount of ligand to a solution of Zeise's dimer at 0 °C; the resulting solution was reduced to a small volume under reduced pressure and the compound precipitated by adding diethyl ether. Both procedures required filtering and washing of the final product under dry nitrogen, otherwise decomposition occurred. The dry product could be safely handled in the air [Found: C, 27.2; H, 5.5; Cl, 15.6; N, 6.4. Calc. for (3a): C, 27.4; H, 5.5; Cl, 16.2; N, 6.4%].

Complex (3a) undergoes a solid-state transformation (in 3—4 weeks at room temperature) to a new form, (3b), having the same composition but different i.r. spectrum and solubility. Whereas (3a) is readily soluble in most organic solvents such as acetone and chloroform, (3b) is almost insoluble in these solvents. In contact with chloroform, however, it slowly dissolves giving a solution, from which (3a) can be precipitated, with some decomposition. Complex (3b) can be prepared by adding the amine (1 mmol) to a methanol solution (10 cm^3) of Zeise's salt (1 mmol) containing HCl (0.5 mmol); the solution was left to stand at room temperature for 12 h, whereupon (3b) separated as a yellow solid [Found: C, 27.0; H, 5.2; Cl, 16.0; N, 6.1. Calc. for (3b): C, 27.4; H, 5.5; Cl, 16.2; N, 6.4%].

Apparatus.—The i.r. spectra in the range 300—4 000 cm^{-1} were recorded as KBr pellets on a Perkin-Elmer 457 spectrophotometer; spectra in the range 100—500 cm^{-1} were obtained from Polythene pellets on a Perkin-Elmer 180 instrument. The ^{1}H n.m.r. spectra were determined with Varian EM 390 and NV 14 spectrometers using $CDCl_3$ as solvent and tetramethylsilane as internal standard. Ultraviolet and visible spectra were recorded on a Perkin-Elmer 575 spectrophotometer. Rates of decomposition were obtained from plots of ln ($A_t - A_\infty$) against time, where A_t and A_∞ are absorbances at time *t* and after at least six half-lives respectively.

RESULTS AND DISCUSSION

All the diamines (L) considered gave, by reaction with Zeise's salt, or its dimer, complexes of composition

$[Pt(C_2H_4)Cl_2L]$. The complexes with Me_4en, (1), and Me_4pn, (2), both in solution and in the solid state, release ethylene to form the square-planar $[PtCl_2L]$ species. The complex $[Pt(C_2H_4)Cl_2(Me_4bn)]$ is obtainable in two different forms, (3a) and (3b), none of which releases ethylene to give the four-co-ordinate $[PtCl_2(Me_4bn)]$ species.

Hydrogen-1 *N.M.R. Spectra*.—The spectra of the complexes and the free ligands are collected in the Table. The spectrum of (1), over the range of temperature explored (−30 to +10 °C), indicates a five-co-ordinate trigonal-bipyramidal structure with the two ends of the ligand occupying equivalent (equatorial) sites. Both the methyl and methylene protons of the ligand show coupling with the ^{195}Pt nucleus (15 and 11 Hz respectively) and the downfield shifts, with respect to the free ligand, are 0.58 and 0.33 p.p.m. respectively. The ethylene protons appear as a triplet [*J*(Pt–H) 69 Hz] centred at 3.37 p.p.m.; the chemical shift and coupling constant are characteristic of a five-co-ordinate species.[1-3,10]

Proton chemical shifts[a] (δ/p.p.m., downfield from $SiMe_4$) of $[Pt(C_2H_4)Cl_2(L)]$ complexes. Values for free L are also included for comparison. Coupling constants (Hz) with ^{195}Pt are given in parentheses

Compound	θ_c/°C	C_2H_4	N–CH_3	N–CH_2–C	C–CH_2–C
Me_4en	30		2.24	2.38	
$[Pt(C_2H_4)Cl_2(Me_4en)]$	−30	3.37(69)	2.82(15)	2.71(11)	
Me_4pn	30		2.22	2.29	1.62
$[Pt(C_2H_4)Cl_2(Me_4pn)]$	30	4.10(66)	2.62	2.80	1.97
	−30	3.51(70)	2.70(13)	2.9(br)	2.0(br)
Me_4bn	30		2.21	2.25	1.46
$[Pt(C_2H_4)Cl_2(Me_4bn)]$	30	4.69(61)	2.62	2.80	1.95
	−30	4.69(61)	3.0(br), 2.6(br)	*b*	*b*

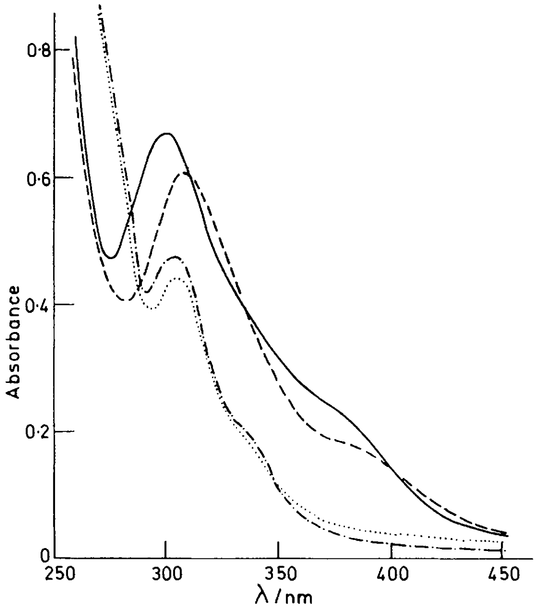
[a] All spectra were recorded in $CDCl_3$ solution; br = broad. [b] Obscured by extensive broadening of the signals.

It is worth noting that the resonance of the ethylene protons is very sensitive to the geometry of the complex and can be diagnostic of either four- or five-co-ordination. For five-co-ordinate complexes the ethylene resonance occurs at higher field and, although the actual value is also dependent on the other ligands present in the molecule, the lower limit is at 3.5—3.6 p.p.m. downfield from $SiMe_4$. For square-planar complexes the ethylene resonance occurs at much lower field and the upper limit can be placed as 4.5—4.6.[11,12]

Complex (2) in $CDCl_3$ solution at −30 °C has an essentially five-co-ordinate structure with the triplet of the ethylene protons centred at 3.51 p.p.m. [*J*(Pt–H) 70 Hz] and that of the methyl protons at 2.70 p.p.m. [*J*(Pt–H) 13 Hz]. As the temperature is increased (from −20 °C) the signals broaden, the triplet of the ethylene protons moves gradually towards lower field, and the NMe protons lose their coupling with platinum. The signals become sharp again at 30 °C. The four methyl groups give a sharp singlet at 2.62 p.p.m. indicating that both ends of the diamine are equivalent on the n.m.r. time scale. The ethylene protons give a triplet centred at 4.10 p.p.m. [*J*(Pt–H) 66 Hz]. These values of chemical shift and coupling constant are intermediate between those of the five-co-ordinate species and those expected for a four-co-ordinate complex. {Values for some *trans*-$[Pt(C_2H_4)Cl_2L]$ complexes are: 4.74 p.p.m., *J*(Pt–H) 63 Hz, for L = *N*-methylmorpholine; 4.68 p.p.m., *J*(Pt–H) 60 Hz, for L = methylamine.} A fluxional behaviour of the Me_4pn ligand between a uni- and bi-dentate form could account for the equivalence of the NMe groups and loss of their coupling with platinum; moreover the average co-ordination about the metal would be intermediate between four and five in full agreement with the chemical shift of the ethylene resonance. An interchange between four- and five-co-ordination could also be attained by reversible dissociation of a chloride ion from the five-co-ordinate species to give $[Pt(C_2H_4)Cl(N–N)]^+(Cl^-)$. However, the formation of such a cationic complex (or an isomer with equivalent ends of the diamine) in $CHCl_3$ is not supported by conductivity measurements; moreover, the extreme reactivity of the ethylene in such a cationic species would readily lead to its substitution or the formation of addition products.[13,14]

The complex $[Pt(C_2H_4)Cl_2(Me_4bn)]$ could be isolated in two different forms, (3a) and (3b), having different i.r. spectra and solubility. Form (3a), which is readily soluble in chloroform, is slowly transformed in the solid state into (3b). The ^1H n.m.r. spectrum at 30 °C of a freshly prepared sample of (3a) shows a triplet for the ethylene protons, whose chemical shift and coupling constant with ^{195}Pt (4.69 p.p.m., 61 Hz) are characteristic of a four-co-ordinate structure. The NMe protons of the diamine give a singlet at 2.62 p.p.m. and do not show any coupling with the platinum nucleus. Since a chloroform solution of this complex at room temperature is not conducting, we suggest that the four-co-ordinate complex contains unidentate diamine, the two ends of which become equivalent through a rapid head-to-tail rearrangement. The average co-ordination about the central metal, however, is still practically four, not intermediate between four and five as in (2), indicating that the configuration with only one end of the ligand bonded to the metal is energetically much more favoured than that with both ends of the ligand co-ordinated. On decreasing the temperature all signals broaden and at −30 °C (at lower temperature the complex precipitates) the ethylene still appears as a triplet centred at 4.69 p.p.m. [*J*(Pt–H) 61 Hz]. However, its intensity is about half that expected. The NMe resonance, originally at 2.62 p.p.m., is split into two broad signals of nearly equal intensity centred at 2.6 and 3.0 p.p.m.

Therefore, the formation at low temperature of a five-co-ordinate species with both ends of the diamine bonded to the metal is not supported by an upfield shift of the ethylene resonance. The presence of the original resonance at 4.69 p.p.m. indicates an η-ethylene ligand in a four-co-ordinate complex containing unidentate diamine, the two ends of which are no longer equivalent on the n.m.r. time scale. The reduced intensity of the ethylene resonance can be explained by assuming a partial $\eta\rightarrow\sigma$ rearrangement of the olefin consequent upon nucleophilic attack by a free end of the diamine; this could also account for the appearance of a NMe resonance at significantly lower field.[12]



Absorption spectra of 5 × 10^{-4} mol dm^{-3} solutions of $[Pt(C_2H_4)Cl_2(Me_4en)]$ (——), $[Pt(C_2H_4)Cl_2(Me_4pn)]$ (— — —), $[Pt(C_2H_4)Cl_2(Me_4bn)]$ (· · · ·), and *trans*-$[Pt(C_2H_4)Cl_2$(*N*-methylmorpholine)] (— · — · —) in 1,2-dichloroethane at 20 °C

The behaviour of complex (3a), in $CDCl_3$ solution, can be related to the behaviour in the solid state. We observed that (3a) undergoes a slow solid-state transformation (3—4 weeks at room temperature) to a new form, (3b). The most significant differences in the i.r. spectra of (3a) and (3b) are found in the region between 900 and 1 000 cm^{-1}. In this region (3b) has two medium-strong absorption bands (at 930 and 960 cm^{-1}) which are not present for (3a) nor for the free amine. Absorption bands of similar intensity and wavenumber are found in the spectra of a series of quaternary ammonium salts and are thought to be related to ν(C–N) stretchings.[15] It seems that the η-ethylene, which is presumably present in (3a), undergoes nucleophilic attack by a free end of the diamine to give a zwitterionic species, (3b). The nucleophilic attack could be either inter- or intramolecular. The proposed zwitterionic structure for (3b) would agree both with the behaviour of (3a) at low temperature in $CDCl_3$ solution and with the fact that (3b) does not show any tendency to release ethylene.

Ultraviolet and Visible Spectra.—The different behaviour of (1)—(3) is also reflected by their u.v. and visible spectra and by their rates of decomposition. Complexes (1) and (2), see Figure, have quite similar spectra (in 1,2-dichloroethane solution) and these differ substantially from that of (3), which resembles the spectra of four-co-ordinate complexes with unidentate aliphatic amines, *e.g.* *trans*-$[Pt(C_2H_4)Cl_2$(*N*-methylmorpholine)]. The rate constant ($k_{obs.}$) for decomposition of (1) to $[PtCl_2(Me_4en)]$ and ethylene is 1×10^{-3} s^{-1} in 1,2-dichloroethane at 20 °C. Complex (2) also decomposes to $[PtCl_2(Me_4pn)]$ and C_2H_4 but at a much lower rate, $k_{obs.} = 2 \times 10^{-5}$ s^{-1}, under analogous conditions. In contrast, (3) is stable in 1,2-dichloroethane solution over several days and on standing for longer periods it decomposes to platinum metal. It is to be noted that formation of a seven-membered chelate ring occurs with difficulty in platinum(II) substrates.[16]

In conclusion it appears that, although a five-membered chelate ring in a five-co-ordinate geometry is characterized by an exceptionally small N–Pt–N angle,[3] it is much more effective in stabilizing five-co-ordination than six- and seven-membered rings which should be capable of forming larger N–Pt–N angles. It is also shown that as the tendency of the N–N ligand to stabilize the five- relative to four-co-ordination increases ($Me_4bn < Me_4pn < Me_4en$), the rate of decomposition of the adduct to give $[PtCl_2(N{-}N)]$ and ethylene also increases. This is what would be expected if the five-co-ordinate species is considered as the intermediate stage in the replacement of ethylene by the second end of the diamine, and gives an unusually clear picture of the mechanism and energetics involved in substitution at a square-planar substrate.

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