# Isolation and Characterisation of Aquo- and Phenyl-(diethylenetriamine)-platinum(II) Complexes

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The preparation and properties of the complex $[Pt(dien)H_2O](ClO_4)_2$ (dien = diethylenetriamine) are described. Studies of the thermodynamics of displacement of the aquo-ligand in the complex by anionic ligands indicate a stability order of hydroxide > halide > benzenesulphonate > propionate. The complex reacts with sodium tetraphenylborate in aqueous solution at room temperature to give $[Pt(dien)Ph]BPh_4$. Electronic spectra of $[Pt(dien)X]^+$ complexes yield a spectrochemical series of $I^- < Br^- < Cl^- < H_2O < Ph^- < OH^-$ for ligands (X) co-ordinated to platinum(II).

KINETICS of substitution reactions of platinum(II) complexes have been widely studied[1-5] and shown to involve the two-term rate equation (1), where L =

$$k_{obs} = (k_1 + k_2[L])[Pt^{II}] \qquad (1)$$

entering ligand and $Pt^{II}$ = substrate. It has generally been assumed that $k_1$ corresponds to a route involving an intermediate complex with the solvent, whereas $k_2$ corresponds to an associative route involving an intermediate in which both the entering and leaving ligands are bound simultaneously to the platinum atom. In spite of the widespread implication of solvent complexes in platinum(II) substitution reactions, few have been isolated and no aquo-platinum(II) complexes appear to have been fully characterised.

As part of a general interest in inorganic reaction mechanisms we set out to completely characterise the replacement of one ligand (X) by another (L) from $[Pt(dien)X]^+$ cations (dien = diethylenetriamine, $NH_2CH_2CH_2NHCH_2CH_2NH_2$. This reaction has been investigated previously,[6-16] but generally only by following the time dependence of the concentration of one of the species present. As part of a complete study of the system we required to isolate and characterise the

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aquo-cation $[Pt(dien)H_2O]^{2+}$. Although this cation has been prepared in solution it has not previously been isolated, probably because it forms complexes that are very soluble in water with most common anions such as nitrate, sulphate, perchlorate, tetrafluoroborate, phosphate, and hexafluorophosphate, and only appears to be precipitated by tetraphenylborate ions. However, the product of reaction with the latter is not the expected $[Pt(dien)H_2O](BPh_4)_2$, but rather the phenyl complex $[Pt(dien)Ph]BPh_4$.

## RESULTS AND DISCUSSION

*Aquo-complex*, $[Pt(dien)(H_2O)](ClO_4)_2$.—The complex was prepared by treating one equivalent of an aqueous solution of the complex [Pt(dien)I]I with two equivalents of silver(I) perchlorate and carefully evaporating the filtrate after the silver(I) iodide had been filtered off. Two possible alternative formulae were considered and rejected: (i) $[Pt(dien)ClO_4]ClO_4$ which is inconsistent with the analytical data, the molar conductivity of 211 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ in acetone at a complex concentration of $10^{-4}$M (typical of a 2 : 1 electrolyte[17]), and the i.r. spectrum (which indicates the presence of water); and (ii) $[Pt(dien)ClO_4]ClO_4,H_2O$ which is inconsistent with the molar conductivity and i.r. spectral data. The i.r. spectra of [Pt(dien)X]Y complexes in the N–H stretching and deformation regions are strongly dependent on the nature of X (see Table 1). The steady increase in $\nu(NH_2)$ and $\nu(NH)$ as the ligand X is varied over the series I < Cl < Ph might, following earlier workers,[18,19] be taken to be indicative of a decrease in the Pt–N bond strength in the $[Pt(dien)X]^+$ cations which parallels the increase in the $\sigma$-donor ability of these ligands in the order X = I < Cl < Ph. Since the $\sigma$-donor ability of the perchlorate ion must be very low, in view of its well known reluctance to co-ordinate to Lewis acids, it can be predicted that both $\nu(NH_2)$ and $\nu(NH)$ in the hypothetical complex $[Pt(dien)ClO_4]ClO_4,H_2O$ would lie below their values in [Pt(dien)I]I. The fact that in the present complex they lie well above those of $[Pt(dien)Ph]BPh_4$ is consistent with its formulation as the doubly charged cationic complex $[Pt(dien)H_2O]^{2+}$-$2ClO_4^-$.

TABLE 1

I.r. spectra of dien complexes of platinum and palladium in the regions 4000—3000 and 1700—1500 cm$^{-1}$

| | Absorption bands (cm$^{-1}$) | | | | |
|---|---|---|---|---|---|
| Complex | $\nu$(O–H) | $\nu(NH_2)$ | $\nu$(NH) | $\delta$(OH) | $\delta(NH_2)$ |
| [Pt(dien)I]I | | 3185,<br>3115 | 3055 | | 1592 |
| $[Pt(dien)Cl]ClO_4$ | | 3232,<br>3192 | 3105 | | 1610,<br>1580 |
| $[Pt(dien)Ph]BPh_4$ | | 3250,<br>3225 | 3190 | | 1580,<br>1575 |
| $[Pt(dien)H_2O]$-$(ClO_4)_2$ | 3500 | 3282,<br>3240 | 3182 | 1630 | 1600,<br>1590 |
| [Pd(dien)Cl]Cl [a] | | 3200,<br>3135 | 3060 | | 1605,<br>1598 |
| [Pd(dien)Br]Br [a] | | 3210,<br>3135 | 3065 | | 1598,<br>1592 |
| [Pd(dien)I]I [a] | | 3200,<br>3205,<br>3130 | 3075 | | 1589 |

[a] From ref. 9.

A solution of the complex $[Pt(dien)H_2O](ClO_4)_2$ in water is measurably acidic because of equilibrium (2).

$$[Pt(dien)H_2O]^{2+} \overset{K_2}{\rightleftharpoons} [Pt(dien)OH]^+ + H^+ \quad (2)$$

The u.v. spectra of such solutions in 0·1M-sodium perchlorate showed three isosbestic points at 290, 264, and 244 nm as the pH was varied between 2·4 and 10·1, which strongly suggests the presence of only two absorbing species, namely the aquo- and hydroxo-complexes. Below pH 2·4 and above pH 10·1 there were no further changes in the spectrum indicating that equilibrium (2) lies virtually completely to the left and right respectively at these two pH values. At 25·2 °C, p$K_2$ in aqueous 0·1M-sodium perchlorate solution was found by titration to be 6·13. Very few hydroxo-complexes of platinum(II) have been isolated and it has been suggested[20] that this is because the typically class 'b' platinum(II) ion[21] cannot form very strong bonds to hydroxide ions. However, the present result, combined with earlier results for the halide ions, shows that hydroxide ions are thermodynamically better ligands for platinum(II) than chloride or bromide ions; there are other systems in the literature that support the present results (see Table 2). It is, however, noteworthy that the ratios of the stability constants for hydroxide and halide ions ($K_{OH} : K_{Cl}$ or $K_{OH} : K_{Br}$) do decrease slightly when platinum is surrounded by softer ligands [*e.g.* both $K_{OH} : K_{Cl}$ and $K_{OH} : K_{Br}$ decrease as the three inert ligands increase in softness from chloride through dien to bromide (Table 2)], giving some support to the earlier contention that the presence of other hard ligands enhances the co-ordination of hard hydroxide ligands (symbiosis).

Equilibrium constants ($K_3$) for the reaction of two further ligands, benzenesulphonate and propionate, that appear to co-ordinate weakly to platinum(II), were determined by measuring $K_4$ in 0·1M-aqueous sodium perchlorate solution at 25·2 °C and calculating

$$[Pt(dien)H_2O]^{2+} + X^- \overset{K_3}{\rightleftharpoons} [Pt(dien)X]^+ + H_2O \quad (3)$$

$$[Pt(dien)H_2O]^{2+} + HX \overset{K_4}{\rightleftharpoons} [Pt(dien)X]^+ + H_3O^+ \quad (4)$$

$K_3$ from the p$K_a$ values of the acids. The calculated $K_3$ values $8{\cdot}27 \times 10^{-3}$ ($X = PhSO_3$) and $8{\cdot}44 \times 10^2$ l mol$^{-1}$ ($X = EtCO_2$) indicate that propionate ions are fairly good ligands for platinum(II), forming complexes

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of comparable stability to chloride ions, whilst benzenesulphonate ions are very poor ligands forming less stable complexes than water.

*Phenyl Complexes.*—All attempts to isolate the aquo-complex $[Pt(dien)H_2O]^{2+}$ as the tetraphenylborate led, not to the expected product $[Pt(dien)H_2O](BPh_4)_2$, but rather to $[Pt(dien)Ph]BPh_4$, formed by reaction (5). This reaction, which is analogous to other arylations

$$[Pt(dien)H_2O]^{2+} + 2BPh_4^- \longrightarrow [Pt(dien)Ph]BPh_4 + H_2O + BPh_3 \quad (5)$$

by tetraphenylborate salts,[22-24] occurs instantaneously on mixing the two aqueous solutions at room temperature in the presence of air and thus provides a very convenient preparation for aryl complexes.

TABLE 2

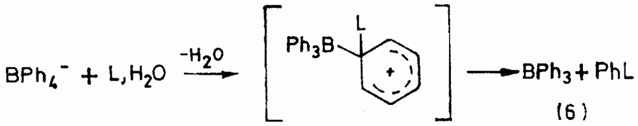
Equilibrium constants at 25 °C for platinum(II) complexes with chloride, bromide, and hydroxide ligands

| | $\frac{K}{\text{l mol}^{-1}}$ | | | | | |
|---|---|---|---|---|---|---|
| Equilibrium | X = OH | X = Cl | X = Br | $K_{OH}/K_{Cl}$ | $K_{OH}/K_{Br}$ | Ref. |
| $[Pt(dien)H_2O]^{2+} + X^- \rightleftharpoons [Pt(dien)X]^+ + H_2O$ | $7{\cdot}4 \times 10^7$ [a] | $5{\cdot}1 \times 10^3$ [a] | $1{\cdot}05 \times 10^4$ [b] | $1{\cdot}45 \times 10^4$ | $7{\cdot}05 \times 10^3$ | This work, 11, 16 |
| $[PtCl_3(H_2O)]^- + X^- \rightleftharpoons [PtCl_3X]^{2-} + H_2O$ | $1{\cdot}0 \times 10^7$ [b] | 54 [b] | 780 [b] | $1{\cdot}85 \times 10^5$ | $1{\cdot}3 \times 10^4$ | *c, d* |
| $[PtBr_3(H_2O)]^- + X^- \rightleftharpoons [PtBr_3X]^{2-} + H_2O$ | $1{\cdot}26 \times 10^6$ [b] | 256 [b] | 380 [b] | $4{\cdot}9 \times 10^3$ | $3{\cdot}3 \times 10^3$ | *d, e* |

[a] $I = 0{\cdot}1$M. [b] $I = 0{\cdot}318$M. [c] L. F. Grantham, T. S. Elleman, and D. S. Martin, *J. Amer. Chem. Soc.*, 1955, **77**, 2965. [d] W. W. Dunning and D. S. Martin, *J. Amer. Chem. Soc.*, 1959, **81**, 5566. [e] J. E. Teggins, D. R. Gano, M. A. Tucker, and D. S. Martin, *Inorg. Chem.*, 1967, **6**, 69.

The phenyl complex was characterised as follows. (i) Chemical analysis and conductivity measurements. (ii) Although the complex $[Pt(dien)Ph]BPh_4$ was too insoluble for n.m.r. study, precipitation of the tetraphenylborate salt with caesium chloride yielded the chloride salt which, after extraction into $(CD_3)_2CO$, had an integrated n.m.r. spectrum (see Experimental section) consistent with the formula $[Pt(dien)Ph]Cl$, the five low-field protons being assigned to the phenyl resonances and the eight high-field protons to the methylene resonances. (iii) The i.r. spectrum of the chloride salt was consistent with the presence of a phenyl group; that of the tetraphenylborate salt showed bands at 1430s, 1458m, and 1480s $cm^{-1}$ characteristic of the tetraphenylborate ion ($NaBPh_4$ exhibits bands at 1430s, 1457m, and 1482s $cm^{-1}$). Recent reports of iridium(I)[25] and rhodium(I)[25,26] complexes containing $\pi$-bonded tetraphenylborate ions prompted us to examine our spectra closely for such species. However, there was no evidence for $\pi$-bonded tetraphenylborate in the present complex.

Although it is perhaps premature to comment on the mechanism of the reaction of the $[Pt(dien)H_2O]^{2+}$ complex with tetraphenylborate ions, a route similar to that established for the acid decomposition of tetraphenylborate ion to benzene and triphenylboron[27] is certainly consistent with the observed products {reaction (6) where L = $H^+$ or $[Pt(dien)]^{2+}$}.



(6)

*Electronic Spectra.*—The positions of the principle bands in the electronic spectra of $[Pt(dien)X]^+$ complexes (Table 3) yield a spectrochemical series of $I^- < Br^- < Cl^- < H_2O \lesssim Ph^- < OH^-$ for ligands co-ordinated to platinum(II). This is essentially the same as that found for other metal ions[28] with the exception that the positions of water and hydroxide ion are inverted. This inversion probably arises from the different charge on the aquo-complex relative to the others in the series, although an anomalous spectrochemical shift has been reported for hydroxo-complexes of platinum(IV).[29]

TABLE 3

Electronic spectra of [Pt(dien)X]Y complexes in aqueous solution in the range 20 000—44 000 $cm^{-1}$

| | | Principal band | | |
|---|---|---|---|---|
| X | Y | $\frac{\bar{\nu}}{cm^{-1}}$ | $\frac{\varepsilon\ ^a}{\text{l mol}^{-1}\ cm^{-1}}$ | Other bands ($cm^{-1}$) |
| Cl | Cl | 37 900 | 261 | 28 650vw,sh |
| Br | Br | 36 360 [b] | | |
| I | I | 33 200 | 465 | 28 800w,sh |
| $H_2O$ | $2 \times ClO_4$ | 41 670 | 410 | 32 360sh |
| Ph | Cl | 41 750 [c] | 12 570 | 39 600,[d] 38 200,[d] 37 300 [d] |
| $OH^-$ | $ClO_4$ | 42 020 | 438 | 39 220sh |

[a] ε = Extinction coefficient. [b] Ref. 7. [c] The solvent was ethanol (90%)–water (10%). [d] Sharp bands were assigned to the phenyl group by comparison with the spectrum of chlorobenzene.

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## EXPERIMENTAL

*Preparation of the Complexes.*—[Pt(dien)I]I. The complex was prepared as described previously[12] with the modification that, after $PtI_2$ was digested with diethylenetriamine, the solution was treated with animal charcoal and filtered to remove any traces of colloidal platinum present before crystallisation (Found: C, 8·8; H, 2·3; N, 7·6. $C_4H_{13}I_2N_3Pt$ requires C, 8·7; H, 2·4; N, 7·6%).

[Pt(dien)Cl]$ClO_4$. The complex was prepared by stirring (16 h) in the absence of light a suspension of [Pt(dien)I]I (2·00 g, 3·6 mmol), silver(I) perchlorate (1·486 g, 7·2 mmol), and hydrochloric acid (12 mmol) in water (50 ml). After the volume was reduced to *ca.* 10 ml on a steam-bath, the solution was cooled in ice to yield colourless *platelets* in 90% yield (Found: C, 11·15; H, 2·9; N, 10·0. $C_4H_{13}Cl_2N_3O_4Pt$ requires C, 11·1; H, 3·0; N, 9·7%).

[Pt(dien)$H_2O$]$(ClO_4)_2$. The complex was prepared by stirring a suspension of [Pt(dien)I]I (0·20 g, 0·36 mmol) and silver(I) perchlorate (0·1486 g, 0·72 mmol) in water (20 ml) for 16 h in the absence of light. After the precipitated silver(I) iodide was filtered off, the volume of the solution was reduced to *ca.* 5 ml on a steam-bath and the solution was then treated with animal charcoal, to remove traces of colloidal platinum, before slow crystallisation at room temperature to give pale yellowish-brown crystals in 95% yield. On heating the *crystals* turned deep orange at 192 °C and melted at 204 °C (Found: C, 9·15; H, 2·8; N, 8·3. $C_4H_{15}Cl_2N_3O_9Pt$ requires C, 9·3; H, 2·9; N, 8·15%).

[Pt(dien)Ph]$BPh_4$. The complex was prepared by treating a solution of [Pt(dien)$H_2O$]$(ClO_4)_2$ with slightly more than 2 equivalents of sodium tetraphenylborate. The fluffy white *precipitate*, which formed instantly, was stirred (4 h) to minimise the occlusion of impurities before being filtered off, washed with water, and dried *in vacuo*. Yield 90%. M.p. *ca.* 190 °C (decomp.) (Found: C, 59·0; H, 5·5; N, 6·15. $C_{34}H_{38}BN_3Pt$ requires C, 58·9; H, 5·5; N, 6·1%).

[Pt(dien)Ph]Cl. The complex was prepared by treating a solution of [Pt(dien)Ph]$BPh_4$ (0·0980 g, 0·141 mmol) in ethanol with a solution of caesium chloride (0·1258 g, 0·748 mmol) in aqueous ethanol and filtering off the fine precipitate of caesium tetraphenylborate. After the solvent was removed the product was extracted with acetone, which was subsequently removed by evaporation to yield a pale yellow *solid*. An integrated n.m.r. spectrum in $(CD_3)_2CO$ showed peaks at 2·28 (2·0 protons), 2·66 and 2·77 (3·1 protons), and 6·75 and 6·87 p.p.m. (7·8 protons) relative to TMS at 10 p.p.m.

[Pt(dien)py]$BPh_4$. This complex was prepared as described previously.[6]

*Determination of the* p$K_a$ *Values of the Complex* [Pt(dien)$H_2O$]$(ClO_4)_2$ *and Propionic Acid.*—A solution of the complex [Pt(dien)$H_2O$]$(ClO_4)_2$ ($1·79 \times 10^{-3}$M) in aqueous sodium perchlorate solution (0·0917M; total ionic strength = 0·1M) thermostatted at 25·2 °C was titrated against a sodium hydroxide solution (0·1M) using a Radiometer type 4 pH meter. The p$K_a$ (6·13) was obtained both directly from the half-equivalence point and by comparing the experimental curve with one calculated using the computer program ACID–BASE.* The p$K_a$ of propionic acid, measured under identical conditions, was found to be 4·75.

*Determination of the Equilibrium Constants for the Reaction:* $[Pt(dien)H_2O]^{2+} + HX \rightleftharpoons [Pt(dien)X]^{+} + H_3O^{+}$ ($X = PhSO_3$ or $EtCO_2$).—Standard ($10^{-2}$M) aqueous solutions of propionic and benzenesulphonic acids were prepared, the former from commercial propionic acid and the latter from benzenesulphonic acid prepared by passing a solution of sodium benzenesulphonate down a Dowex 50W-X8 cation-exchange resin (this procedure was necessary because the available commercial acid contained a significant quantity of iron). The standard acid solution (5 ml), a solution of the complex [Pt(dien)$H_2O$]$(ClO_4)_2$ (5 ml, $8·97 \times 10^{-3}$M), chloride-free sodium perchlorate (0·45 ml, 5·55M; prepared from AnalaR perchloric acid and AnalaR anhydrous sodium carbonate[30]), and distilled water (14·55 ml) were added to a two-necked flask (50 ml) immersed in a constant-temperature water-bath (Grant Instruments) maintained at 25·2 ± 0·05 °C. After the mixture was equilibrated (72 h), it was titrated against standard 0·1M-sodium hydroxide solution using a Radiometer type 4 pH meter which had been standardised against a potassium hydrogen phthalate buffer solution. Using the p$K_a$ values 0·70 ($PhSO_3H$),[31] 4·75 ($EtCO_2H$) (see above), and 6·13 {$[Pt(dien)H_2O]^{2+}$} (see above), equilibrium constants ($K_4$) for reaction (4), at 25·2 °C in 0·1M-aqueous sodium perchlorate solution, were calculated to be $1·65 \times 10^{-3}$ ($X = PhSO_3$) and $1·50 \times 10^{-2}$ ($X = EtCO_2$).

The molar conductivities of solutions ($10^{-4}$M) of the complexes [Pt(dien)Ph]$BPh_4$ and [Pt(dien)py]$(BPh_4)_2$ in redistilled nitrobenzene at 20 °C, measured using a Phillips PR 9500 conductivity bridge, were 16·2 and 33·3 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ respectively, confirming that the complex [Pt(dien)Ph]$BPh_4$ is a 1 : 1 electrolyte. Since the complex [Pt(dien)$H_2O$]$(ClO_4)_2$ was insoluble in nitrobenzene, its molar conductivity was determined in acetone and was found to be 211 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ at a complex concentration of $10^{-4}$M; this conductivity value is typical of a 2 : 1 electrolyte.[17]

Electronic spectra were recorded on a Unicam SP 800 spectrophotometer, i.r. spectra in Nujol and hexachlorobutadiene mulls on Perkin-Elmer model 337 and Unicam SP 200G spectrometers, and n.m.r. spectra on a Perkin-Elmer R12 spectrometer. Microanalyses were carried out by the microanalytical department at University College, London.

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* To be described elsewhere.

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