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A FAST ATOM BOMBARDMENT MASS SPECTROMETRIC INVESTIGATION OF SOME TRIETHYLPHOSPHINE COMPLEXES OF PLATINUM(II) IN AQUEOUS SOLUTION

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Summary

Fast atom bombardment (FAB) mass spectrometry was used to probe aqueous solutions containing equilibrium mixtures of triethylphosphine complexes of Pt^{II}, and allowed some elucidation of the nature of the equilibria. The study shows the potential of FAB for investigation of equilibrated systems in solution.

We have previously shown that near UV photolysis of aqueous solutions of $[PtH(PEt_3)_3]^+$ produces hydrogen and a Pt^{II} species formulated as $[PtY(PEt_3)_3]^{n+}$ ($Y = HSO_4$, $n = 1$; $Y = H_2O$, $n = 2$) [1–3]. Attempts to identify this complex centred on a series of reactions between *cis*-$[PtCl_2(PEt_3)_2]$, PEt_3 and various silver salts in aqueous solution [4], and showed that complex equilibria are set up between species of the general formula $[PtX(PEt_3)_3]^{n+}$, ($X = H_2O$, $n = 2$; $X = OAc$, NO_3, HSO_4, ClO_4, $n = 1$). We now report details of a fast atom bombardment (FAB) mass spectrometric investigation of some aqueous solutions containing such equilibrated species and show the potential of FAB for elucidation of solution equilibria. Part of this work has appeared as a preliminary communication [5].

Results and discussion

Studies on complexes of the formula $[PtX(PEt_3)_3]^{n+}$, *(*$X = H_2O$, $n = 2$; $X = NO_3$, ClO_4, *OAc, H,* HSO_4, *or Cl,* $n = 1$*)*

The FAB spectra of these complexes (see Fig. 1) are similar, showing ions arising from the loss of PEt_3 from $[PtH(PEt_3)_3]^+$ or $[Pt(PEt_3)_3]^+$ and from the loss of

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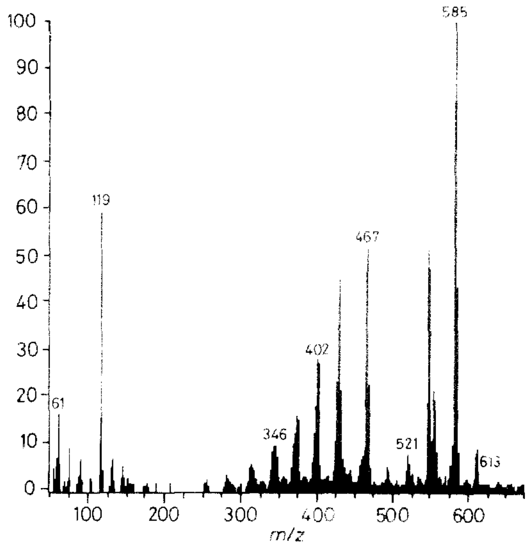

Fig. 1. FAB spectrum of $[PtCl(PEt_3)_3]^+$ in dilute HCl.

ethylene from the triethylphosphine ligands of $[Pt(PEt_3)_2]^+$. One other common feature (from samples where $X = NO_3$, ClO_4, OAc or Cl) is the presence of a fragment of medium to strong intensity corresponding to $[PtX(PEt_3)_2]^+$, formed by loss of PEt_3 from $[PtX(PEt_3)_3]^+$ (see Table 1).

For all of these complexes with the exception of $[PtH(PEt_3)_3]^+$ and $[PtCl(PEt_3)_3]^+$, the molecular ion signal is very weak and this suggests a parallel with the observed [4] aqueous chemistry of these species [6]. All of these complexes (with the exception of $[PtH(PEt_3)_3]^+$) are prepared by reaction of *cis*-$[PtCl_2(PEt_3)_2]$

TABLE 1

SOME COMMONLY OCCURRING FRAGMENTS OF $[PtX(PEt_3)_3]^{n+}$

m/z [a]	Assignment	Intensity range [b] (%)
550/549	$[PtH(PEt_3)_3]^+/[Pt(PEt_3)_3]^+$	100
521	$[Pt(PEt_3)_3 - (C_2H_4)]^+$	6
431	$[Pt(PEt_3)_2]^+$	50–110
402	$[Pt(PEt_3)_2 - (C_2H_4) - H]^+$	25–55
374	$[Pt(PEt_3)_2 - 2(C_2H_4) - H]^+$	18–35
346	$[Pt(PEt_3)_2 - 3(C_2H_4) - H]^+$	10–20
318	$[Pt(PEt_3)_2 - 4(C_2H_4) - H]^+$	7–9
119	$[PEt_3 + H]$	20–70
467	$[PtCl(PEt_3)_2]^+$	60
531	$[Pt(ClO_4)(PEt_3)_2]^+$	45
493	$[Pt(NO_3)(PEt_3)_2]^+$	80
490	$[Pt(OAc)(PEt_3)_2]^+$	25

[a] Throughout the text all signals are quoted with respect to the most abundant peak in the isotope pattern. [b] Intensities are normalised to *m/z* 550 or 549, since the former is the molecular ion signal (for $[PtH(PEt_3)_3]^+$), whilst the latter is the $[M - X]^+$ ion, present in all other spectra.

with PEt_3 in the presence of HX and AgX [4]. For $[PtCl(PEt_3)_3]^+$, the same procedure is followed with the omission of a silver salt. For X = NO_3, ClO_4 and $1/2SO_4$, the ^{31}P NMR spectra of the aqueous solutions are identical (see ref. 4 for all ^{31}P NMR data) suggesting that the Pt–X interaction is quite weak and that complex equilibria exist in solution. When X = OAc, the ^{31}P NMR spectrum shows that $[Pt(OAc)(PEt_3)_3]^+$ is the only Pt species in solution and yet FAB shows the molecular ion signal to be very weak at about 5% of the intensity of the $[Pt(PEt_3)_3]^+$ fragment. This would suggest that the Pt–OAc interaction is also weak (linked scan [7] studies (B^2/E - see Experimental) showed that $[Pt(OAc)(PEt_3)_3]^+$ fragments give $[Pt(PEt_3)_3]^+$) although not so weak as for X = NO_3, ClO_4 and $1/2SO_4$.

These observations lend weight to the idea that complex equilibria exist between these various complexes involving exchange of X with solvent water. Furthermore, they show that the individual species are actually present in solution (see Ref. 4, Scheme 1).

For $[PtCl(PEt_3)_3]^+$ the molecular ion is the strongest signal in the spectrum (see Fig. 1), implying that the Pt–Cl interaction may be significantly stronger than the interaction of Pt with NO_3^-, OAc^-, and ClO_4^- in such complexes as only weak molecular ion signals are observed. These interactions are in turn very much stronger than the similar interaction of Pt with H_2O or HSO_4^-, for which no molecular ion signals are observed in solution (although in the solid state [8], $[Pt(H_2O)(PEt_3)_3][PF_6]_2$ shows a quasi-molecular ion signal at m/z 567 ($[M - H]^+$)). Indeed, in dilute HCl, $[PtCl(PEt_3)_3]^+$ undergoes thermal conversion into *cis*- and *trans*-$[PtCl_2(PEt_3)_2]$ and in this case it is a Pt–P bond which is broken [9].

Studies on bis(triethylphosphine)platinum(II) complexes

As previously described [4], reaction of *cis*-$[PtCl_2(PEt_3)_2]$ with Ag^+ in water leads to formation of $[Pt_2(\mu\text{-}OH)_2(PEt_3)_4]^{2+}$ and another complex with two equivalent phosphorus atoms bound to platinum. Acidification of such solutions allows complete conversion into the latter complex. Where the silver salt used is $AgClO_4$, $AgNO_3$, AgOAc or Ag_2SO_4, the ^{31}P NMR spectra of the solutions acidified with the corresponding acid (e.g. $HClO_4$, etc.) are identical. This implies that complex equilibria are again set up between species such as those shown in Fig. 2 for the case of incorporation of nitrate. Thus X is again exchanging with solvent water. FAB studies on solutions prepared for X = NO_3 and $1/2SO_4$ led to some elucidation of these equilibria.

For X = NO_3 the FAB spectrum shows a strong signal at m/z 493 corresponding to $[Pt(NO_3)(PEt_3)_2]^+$, although this species has not so far been isolated. For X = $1/2SO_4$, the signal corresponding to $[Pt(SO_4)(PEt_3)_2 + H]^+$ at m/z 528 is very weak, and this is also true for the spectrum obtained from the pure sample of the

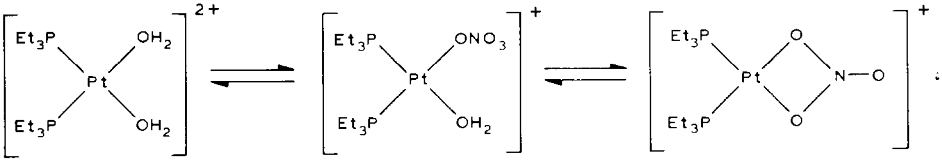

Fig. 2. Possible equilibrium species in solutions produced by reaction of *cis*-$[PtCl_2(PEt_3)_2]$ with $AgNO_3$ in dilute HNO_3.

isolated complex, $[Pt(SO_4)(PEt_3)_2]$ in a chloroform/glycerol matrix. This complex also gives a good electron-impact mass spectrum [8]. That the nitrate complex shows an abundant molecular ion whilst the sulphate complex does not (and it should be borne in mind that only the latter has been isolated) is a result of FAB ionisation which mirrors the aqueous chemistry. The FAB process involves a rapid momentum transfer from the fast Ar (or Xe) atoms to the sample. Therefore ionic species such as $[Pt(NO_3)(PEt_3)_2]^+$ will easily be desorbed from the matrix and detected. However, a neutral complex such as $[Pt(SO_4)(PEt_3)_2]$ will require protonation (to $[Pt(SO_4)(PEt_3)_2 + H]^+$) before it can be detected. Protonation of this latter complex is evidently not easy (or fragmentation is facile), as the quasi-molecular ion signal is always weak; this is supported by the fact that solid $[Pt(SO_4)(PEt_3)_2]$ will not redissolve in acid (from which it is isolated), and is therefore almost certainly present as a solvated complex in solutions from which it is recovered [4]. Neither spectra showed any signals which could be derived from such species as $[Pt(H_2O)_2(PEt_3)_2]^{2+}$ or $[PtX(H_2O)(PEt_3)_2]^+$ ($X = NO_3$ or HSO_4).

By comparison, good FAB spectra are obtained from crystalline samples of $[Pt_2(\mu\text{-}OH)_2(PEt_3)_4][PF_6]_2$, for which two quasi-molecular ions are observed at *m/z* 895 ($[Pt_2(OH)_2(PEt_3)_4 - H]^+$) and *m/z* 1041 ($[Pt_2(OH)_2(PEt_3)_4 + [PF_6]]^+$).

A commonly occurring signal in the spectra of these samples is found at *m/z* 715 and this is assigned to $[Pt_2(PEt_3)_2(PEt_2)]^+$ as a result of a collision-induced [10], *B/E* linked scan experiment, which showed exhaustive loss of C_2H_4 from the $PEt_{3(2)}$ ligands.

Effect of sample / glycerol ratio on spectra

Spectra were obtained for aqueous acidic (HOAc) solutions of $[Pt(OAc)(PEt_3)_3]^+$ using the following sample/glycerol ratios (i) 10/1, (ii) 3/1, (iii) 1/1, (iv) 1/3, (v) 1/10. The samples were run immediately on mixing and then again 24 h later.

The results obtained from the samples run immediately upon mixing show the expected increase in the intensity of the [glycerol + H]$^+$ signal (at *m/z* 93) with decreasing sample/glycerol ratio. The intensity of the signal at *m/z* 93 varied from zero to four times more intense than the most intense sample signal. The results from the same samples run 24 h later are a little more surprising, showing in all cases a dramatic drop in the intensity of the signal at *m/z* 93. This we attribute to better mixing of the sample with the glycerol; the relatively high viscosity of glycerol preventing good mixing for the samples run immediately. Finally, we observed no new cluster ions in the spectra, irrespective both of the glycerol concentration and of the length of time between sample preparation and spectral aquisition.

We found that the spectra were most informative at sample/glycerol ratios of 3/1–1/1.

Effect of different matrices

Spectra were obtained for aqueous acidic (HOAc) solutions of $[Pt(OAc)(PEt_3)_3]^+$ using matrices other than glycerol in an attempt to establish the influence of the matrix on the appearance of the spectra. Sulpholane, as might be expected, showed less evidence of proton transfer, and the spectra seemed to be relatively free from species formed between the matrix and the sample, sulpholane is thus an effective alternative to glycerol. Triethyleneglycol was found to be an unsatisfactory matrix as it dominated the spectra because of its high volatility, and so only weak sample signals were observed.

Spectra obtained in the absence of a matrix were very short-lived and unsatisfactory, despite the ionic nature of the sample.

Summary and conclusions

This series of experiments has told us much about the chemical equilibria under investigation and something about the potential of FAB for the investigation of species in aqueous solution.

The equilibria have proved to be quite complex, and this has been shown to be the result of a weak interaction between Pt and the fourth ligand X (for X = H_2O, ClO_4^-, NO_3^- and HSO_4^-). Thus exchange of X with solvent water is rapid. However, where the Pt–X interaction is strong enough (OAc^-, NO_3^- and ClO_4^-), the equilibrium species is observed in the FAB spectrum, albeit at low signal intensity.

For X = OAc, ^{31}P NMR spectroscopy showed that there was no exchange of X with water, and yet the intensity of the $[Pt(OAc)(PEt_3)_3]^+$ molecular ion was still very low. Hence, even in complexes where the Pt–X interaction is relatively strong, FAB is still sufficiently energetic to induce loss of X from the complex. It is hardly surprising, therefore, that molecular ions are not observed for X = H_2O and HSO_4, since these complexes are difficult to isolate.

In the light of these studies it is possible to say something about the potential of FAB for the examination of solution equilibria or reaction solutions. In these experiments, chemical isolation [4], NMR spectroscopy [4], and FAB have played a complimentary, sometimes overlapping role in the elucidation of these equilibria, giving a better understanding of the processes involved.

FAB itself has proved to be a valuable technique for these systems, and has shown the existence of solution species for which there was no previous direct evidence and in cases in which other spectroscopic techniques were not very informative. Other groups have also commented on the way in which FAB mirrors solution behaviour [6,11,14], but most of the aqueous samples were examined as solutions in glycerol and we have found that the matrix interacts with the sample during atom bombardment. Thus, it is advisable that evaluation and interpretation of data from such experiments should be carried out with caution.

All of the complexes considered in this paper have been of platinum(II), yet some of the species observed by FAB could not really be described as showing this (e.g. $[Pt(PEt_3)_3]^+$ of m/z 549). However, it has been proposed [12] that both electrons and radicals participate during sample desorption and this could explain the "unexpected" formal oxidation states of the metal. Indeed, other authors have found such "unexpected" oxidation states in studies performed on simple salts of the Group IA and IIA metals [13].

Experimental

The preparations of all materials and sample solutions (all typically 10^{-1} to 10^{-2} mol in Pt) and the recording of NMR spectra have been described elsewhere [4]. Analysis by FAB mass spectrometry was performed on a VG Analytical 7070E medium-resolution mass spectrometer. The spectra were obtained in the positive ion mode. Samples were loaded onto the probe as solutions in solvents described in the text at ca. 1 $\mu g\ \mu l^{-1}$ as 1 μl films. Glycerol was used as the matrix unless otherwise stated. The atom gun was operated at 8 kV and Xenon was employed as the bombarding gas.

Linked scanning techniques [7] were employed to study fragmentation in the first field-free region of the spectrometer in order to assign the origin of commonly occurring fragment ions. The linked or combined scan involves two of the spectrometer variables (magnetic (B) and electric (E) fields and accelerating voltage (V)) being scanned simultaneously with a constant relationship. There are two main types of linked scans which provide information:

(i) The B/E scan provides information concerning daughter ions, and
(ii) The B^2/E scan provides information concerning parent ions.

Linked scanning experiments carried out under normal spectrometer operating conditions give information on unimolecular decompositions (i.e. those that would be observed in a normal mass spectrum). When a gas such as dry nitrogen is added to the first field-free region gas cell, some of the translational energy of the ions is converted into internal energy giving rise to enhancement of the fragmentation products. This technique is called "collision-induced dissociation" (C.I.D.) [10].

Reaction of a solution of $[Pt(H_2O)(PEt_3)_3]^{2+}$ *with glycerol*

A solution of $[Pt(H_2O)(PEt_3)_3]^{2+}$ was prepared from *cis*-$[PtCl_2(PEt_3)_2]$, PEt_3 and Ag_2SO_4 in dilute sulphuric acid [4] and its $^{31}P\{^1H\}$ NMR spectrum was recorded. A portion (2 cm^3) of this solution was added to glycerol (2 cm^3) and the mixture was stirred overnight. The $^{31}P\{^1H\}$ NMR spectrum was unchanged, implying that no reaction had occurred. The mixture was then kept at 60°C for 4 h, and again the $^{31}P\{^1H\}$ NMR spectrum implied that no reaction had taken place.

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