Observation of Transition Metal Complexes in Aqueous Solution by Fast Atom Bombardment Mass Spectrometry

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Fast atom bombardment mass spectrometry has been successfully employed for the observation of triethylphosphine complexes of platinum(II) in aqueous solution; in some cases species have been identified in complex equilibrium mixtures, despite their undergoing fast intermolecular exchange.

Since the development of fast atom bombardment (f.a.b.) mass spectrometry,[1,2] the technique has found wide favour with inorganic chemists[3] for two main reasons. First, the method of volatilisation [momentum transfer from fast moving Ar (or Xe) atoms][4] is quite 'soft' when compared with many other mass spectrometric techniques[5] and hence molecular ion signals can be observed for very high molecular weight species (*e.g.*, vitamin B_{12} coenzyme, mass = 1578 g mol^{-1}).[6] Secondly, because volatilisation is primarily due to momentum transfer, ionic species can easily be observed.[3a] To our knowledge, all such spectra have been obtained as mulls of the isolated solid with a support such as glycerol in which the solid is insoluble.‡

However, information about the nature of species *in solution* would be extremely valuable, particularly where complex equilibria which are fast on the n.m.r. time-scale are occurring. We now report that f.a.b. mass spectrometry can provide information on the species present in aqueous solutions of triethylphosphine complexes of platinum(II).

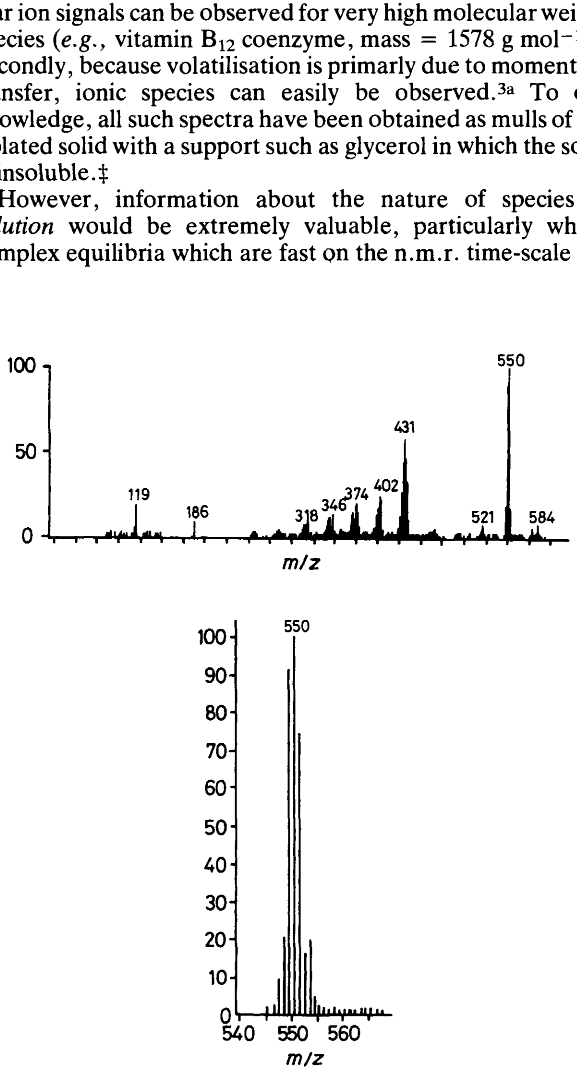

Figure 1. F.a.b. mass spectrum of $[PtH(PEt_3)_3]^+$ in dilute H_2SO_4.

Excellent f.a.b. mass spectra were obtained from mixtures of glycerol (1 μl) and solutions of, *e.g.*, $[PtX(PEt_3)_3]^+$ (~ 10^{-2} mol dm^{-3}; 1 μl) in dilute acids [X = H, in H_2SO_4 (Figure 1); X = Cl, in HCl (Figure 2)]. In common with other f.a.b. mass spectra,[1] these spectra persisted for several minutes without appreciable change.

Parent ions were observed for both of these complexes together with fragments corresponding to $[M-PEt_3]^+$, $[M-X-PEt_3]^+$ and, for X = Cl, $[M-Cl]^+$. Furthermore, successive losses of C_2H_4 from the PEt_3 ligands of $[Pt(PEt_3)_2]^+$ were also observed.

In order to test the possibility of using mass spectrometry to identify species undergoing fast equilibria in solution, we have carried out f.a.b. studies on solutions obtained[7] from reactions of *cis*-$[PtCl_2(PEt_3)_2]$, PEt_3, and 2AgX (X = ClO_4 or $\frac{1}{2}SO_4$) in dilute H_2SO_4. ^{31}P N.m.r. spectra of both solutions are identical and we have proposed[7] that fast equilibria are occurring between $[Pt(H_2O)(PEt_3)_3]^{2+}$, $[Pt(OSO_3H)(PEt_3)_3]^+$, $[\{Pt(PEt_3)_3\}_2SO_4]^{2+}$, and, if ClO_4^- is present, $[Pt(ClO_4)(PEt_3)_3]^+$. Addition of PF_6^- or ClO_4^- allows isolation of $[Pt(H_2O)(PEt_3)_3][PF_6]_2$ (X = $\frac{1}{2}SO_4$) or $[Pt(ClO_4)(PEt_3)_3][ClO_4]$ (X = ClO_4) respectively. F.a.b. mass spectra of the solutions show that the cations $[Pt(H_2O)(PEt_3)_3]^+$, X = $\frac{1}{2}SO_4$ (*m/z* 567), and $[Pt(ClO_4)(PEt_3)_3]^+$, X = ClO_4 (*m/z* 649), are present in solution, since parent ions and appropriate fragmentation patterns are observed. For $[Pt(H_2O)(PEt_3)_3]^{2+}$, the same

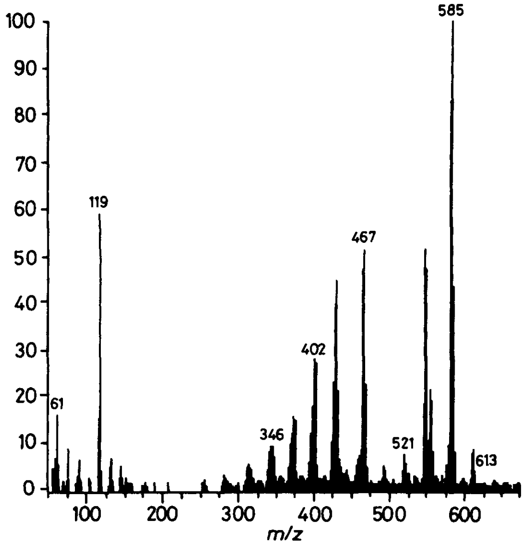

Figure 2. F.a.b. mass spectrum of $[PtCl(PEt_3)_3]^+$ in dilute HCl.

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‡ However, good f.a.b. spectra have been obtained for [Rh(cycloocta-1,5-diene)$\{C_5H_9(CH_2)_3Si(OMe)_3\}$], which is an oil, in the absence of added mixture.[3a]

spectrum is observed from the solid (isolated as its PF_6^- salt) in glycerol.[8] No attempt has yet been made to obtain the f.a.b. spectrum of $[Pt(ClO_4)(PEt_3)_3][ClO_4]$.

We conclude that f.a.b. mass spectrometry may prove an exceptionally powerful tool for the identification of labile species in solution where other spectroscopic techniques are not very informative.

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