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An electrospray mass spectrometric study of some mercury phosphine complexes

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Abstract

Electrospray mass spectra have been obtained for a number of cationic mercury phosphine systems and mixtures thereof in methanol solution. Complexes of the type $Hg(PR_3)_2X_2$ (PR_3 = monodentate phosphine; X = ClO_4, CF_3COO) all give peaks in their electrospray mass spectra corresponding to the principal ion $[Hg(PR_3)_2X]^+$, although with the perchlorates the base peak is due to $[Hg(PR_3)_2(CH_3COO)]^+$, the acetate being present in the mobile phase used in the spectrometer. Many of these systems are known to be labile on the NMR timescale at room temperature, but they all give good electrospray mass spectra at room temperature and for the rapidly exchanging mixtures all of the individual cationic species are observed. Addition of free phosphine leads to the formation of the tris(phosphine) complexes in solution and the principal ions $[Hg(PR_3)_3X]^+$ are observed in the electrospray mass spectra. Collisionally activated decomposition (CAD) mass spectra, both within the ion source and in MS/MS experiments, show that the tris(phosphine) complexes very readily lose one phosphine, thus demonstrating the mechanism of phosphine exchange in these systems.

Introduction

Mercury phosphine complexes have been extensively studied by both ^{31}P and ^{199}Hg NMR spectroscopies [1–7]. In general, one or two phosphines can be added to most $Hg(anion)_2$ compounds, but reaction with further phosphine depends upon the steric demands of the phosphine and the nature of the anion. For example, with tributylphosphine, four phosphine ligands can be detected coordinated to mercury at low temperature using mercury(II) perchlorate, whereas only three phosphine ligands can be coordinated using a wide variety of other anions including the halides, acetate and trifluoroacetate [6]. Mercury cyanide and mercury dithiolates (dithiocarbamates, dithiophosphates etc.) allow coordination of only two tributylphosphine ligands [6, 7]. In most cases the phosphine complexes are labile on the NMR timescale at room temperature and observation of the NMR spectra at low temperatures is usually necessary in order to observe the static spectra and coupling between ^{199}Hg and ^{31}P nuclei. It is often impossible to isolate the phosphine rich species as solids as they undergo dissociation liberating free phosphine.

Electrospray mass spectrometry (ESMS) is a new technique whose use is undergoing rapid exponential growth [8], although its applications to inorganic systems are so far rather few. ESMS allows transfer of pre-existing ions in solution to the gas phase. It is a very soft technique, causing minimal fragmentation, and was first developed to investigate the mass spectra of large molecules of biological interest [9–11].

We have been developing the use of ESMS to investigate inorganic cations and anions in solution and the principal ion is almost always observed for stable species [12–14]. The principal ions are also observed for a wide range of metal carbonyl cations and anions, although loss of carbonyl groups can be observed at higher ion source energies [15]. We have recently discovered that when ESMS is applied to systems which are undergoing rapid ligand exchange on the NMR timescale at room temperature, the technique allows observation of all the exchanging species, provided they are charged [16]. This occurs because the ligand exchange stops immediately when the ions are transferred from solution to the gas phase.

In this paper we report on the application of ESMS to some labile mercury phosphine complexes.

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Results and discussion

Throughout this paper, peaks in the mass spectra will be identified by the most intense *m*/*z* value in the isotopic mass distribution. In all cases the experimental isotopic mass distribution agreed well with the calculated distribution. Results will first be presented for complexes containing only one type of phosphine.

$Hg(ClO_4)_2$ complexes

The electrospray mass spectrum of a 0.2 mM solution of $Hg(pcy)_2(ClO_4)_2$ (pcy = tricyclohexylphosphine) in dichloromethane/methanol (1:10) at an ion source voltage (B1) of 40 V (see 'Experimental') is shown in Fig. 1(a). It shows a strong peak at *m*/*z* 821 due to $[Hg(pcy)_2(CH_3COO)]^+$ and much weaker peaks at *m*/*z* 861 and 381 due to $[Hg(pcy)_2(ClO_4)]^+$ and $[Hg(pcy)_2]^{2+}$, respectively. There is no fragmentation of the ions and the quality of this spectrum is typical of those reported throughout this paper. The acetate complex is derived from the acetic acid present in the mobile phase of the mass spectrometer and its presence as the base peak shows that the perchlorate ion is readily displaced from mercury, which confirms the deductions made from NMR studies [6]. All data for this system and others containing only one type of phosphine are given in Table 1.

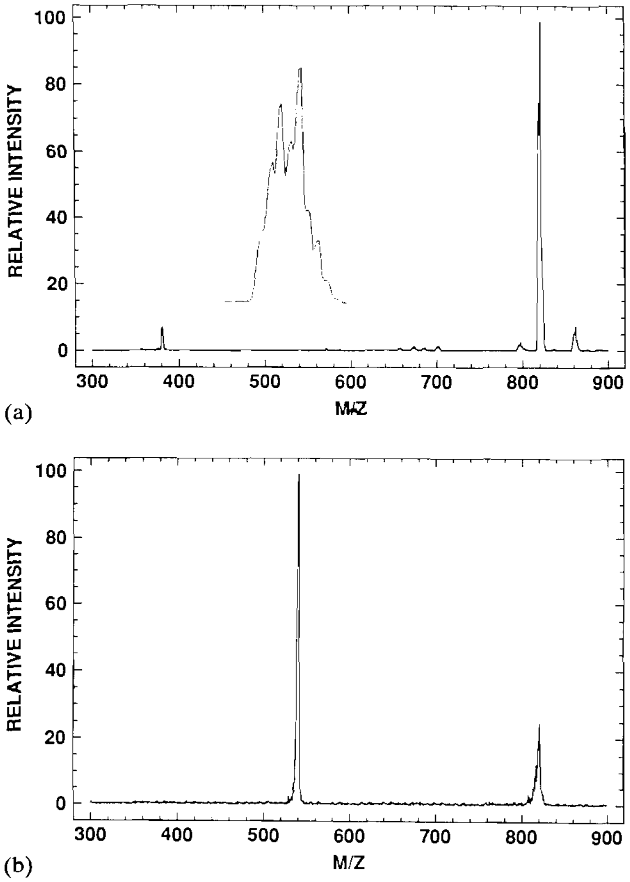

Fig. 1. (a) ES mass spectrum of $Hg(pcy)_2(ClO_4)_2$ (B1 = 40 V). (b) CAD/MS of peak at *m*/*z* 821 (argon, 200 V).

The mass spectrometer used here has the facility to select ions of a particular *m*/*z* value from an isotopic mass distribution from the first mass analyser and pass them through a collision cell into a second mass analyser. In the absence of a gas in the collision cell, ions of *m*/*z* 821 showed no decomposition in the second mass analyser, but in the presence of argon in the collision cell and at an accelerating voltage of 200 V, loss of one phosphine ligand was observed to give $[Hg(pcy)(CH_3COO)]^+$ (*m*/*z* 541) as shown in Fig. 1(b).

Addition of free pcy to the solution gave no indication of the formation of any mercury species containing three pcy ligands, because of the steric demands of the ligand, and this is in agreement with earlier NMR results [6]. Although this is a very simple system, it does illustrate that ESMS can be used at room temperature to study mercury phosphine complexes and gives results complementary to those derived from NMR studies at low temperatures.

The ES mass spectrum of $Hg(ppt)_2(ClO_4)_2$ (ppt = tri-*p*-tolylphosphine) in dichloromethane/methanol (B1 = 50 V) gives strong peaks at *m*/*z* 909, 869 and 565 assigned to $[Hg(ppt)_2(ClO_4)]^+$, $[Hg(ppt)_2(CH_3COO)]^+$ and $[Hg(ppt)(CH_3COO)]^+$, respectively. Weak peaks at *m*/*z* 845 and 541 are also observed which are due to $[Hg(ppt)_2Cl]^+$ and $[Hg(ppt)Cl]^+$. It is thought that these chloro species are generated in the ion source from perchlorate or dichloromethane (which is present at high concentration) in the gas phase. When the ion source voltage (B1) is increased to 70 V the only significant peak is that due to $[Hg(ppt)(CH_3COO)]^+$ (*m*/*z* 565) and when B1 is reduced to 35 V the only significant peak is at *m*/*z* 869 due to $[Hg(ppt)_2(CH_3COO)]^+$. This variation in relative intensities of the peaks is consistent with decomposition of the principal ions caused by collision with solvent molecules in the vicinity of the evaporation nozzle where the pressure is close to atmospheric. Tandem mass spectrometry confirms loss of phosphine ligand from $[Hg(ppt)_2(CH_3COO)]^+$ when argon is present in the collision cell.

Addition of more ppt ligand to the solution of $Hg(ppt)_2(ClO_4)_2$ gave an ES mass spectrum with strong peaks for $[Hg(ppt)_3(CH_3COO)]^+$ (*m*/*z* 1173) and $[Hg(ppt)_3Cl]^+$ (*m*/*z* 1149) and a weaker peak due to $[Hg(ppt)_3(ClO_4)]^+$ (*m*/*z* 1213). Peaks due to the mercury bis(ppt) complexes were also observed and at higher ion source energies their intensities increased relative to those of the mercury tris(ppt) ions. At low B1 voltages a strong peak at *m*/*z* 709 assigned to $[Hg(ppt)_4]^{2+}$ was also observed together with another at *m*/*z* 716 assigned to $[Hg(ppt)_3(pptO)]^{2+}$. Insertion of oxygen to form a

TABLE 1. Electrospray mass spectrometric data for complexes containing one type of phosphine pmt = tri-*m*-tolylphosphine; ppt = tri-*p*-tolylphosphine; pom = tri-*o*-methoxyphenylphosphine; pcy = tricyclohexylphosphine; ppCl = tri-*p*-Clphenylphosphine

Compound	Ions (*m*/*z*)
$Hg(pcy)_2(ClO_4)_2$	$[Hg(pcy)_2ClO_4]^+$ (861); $[Hg(pcy)_2(CH_3COO)]^+$ (821); $[Hg(pcy)_2]^{2+}$ (381)
$Hg(ppt)_2(ClO_4)_2$	$[Hg(ppt)_2(ClO_4)]^+$ (909); $[Hg(ppt)_2(CH_3COO)]^+$ (869); $[Hg(ppt)_2Cl]^+$ (845); $[Hg(ppt)(CH_3COO)]^+$ (565); $[Hg(ppt)Cl]^+$ (541)
$Hg(ppt)_2(ClO_4)_2$ + ppt	$[Hg(ppt)_3(ClO_4)]^+$ (1213); $[Hg(ppt)_3(CH_3COO)]^+$ (1173); $[Hg(ppt)_3Cl]^+$ (1150); $[Hg(ppt)_3(pptO)]^{2+}$ (717); $[Hg(ppt)_4]^{2+}$ (709)
$Hg(pom)_2(CF_3COO)_2$	$[Hg(pom)_2(CF_3COO)]^+$ (1019); $[Hg(pom)(CF_3COO)]^+$ (667); $[Hg(pom)(CH_3COO)]^+$ (613); $[Hg(pom)_2]^{2+}$ (453)
$Hg(pmt)_2(CF_3COO)_2$	$[Hg(pmt)_2(CF_3COO)]^+$ (923); $[Hg(pmt)_2(CH_3COO)]^+$ (869); $[Hg(pmt)(CF_3COO)]^+$ (619); $[Hg(pmt)(CH_3COO)]^+$ (565)
$Hg(pmt)_2(CF_3COO)_2$ + pmt	$[Hg(pmt)_3(CF_3COO)]^+$ (1227)
$Hg(ppCl)_2(CF_3COO)_2$	$[Hg(ppCl)_2(CF_3COO)]^+$ (1045); $[Hg(ppCl)_2(CH_3COO)]^+$ (991)
$Hg(ppCl)_2(CF_3COO)_2$ + ppCl	$[Hg(ppCl)_3(CF_3COO)]^+$ (1411); $[Hg(ppCl)_3(CH_3COO)]^+$ (1349)

phosphine oxide complex has been observed previously [16] and is thought to occur within the ion source. In previous NMR studies [6] we have shown that this system is labile on the NMR timescale at room temperature and we suggested rapid and reversible interchange between mercury bis- and mercury tris(phosphine) ligand complexes as the exchange mechanism. These ESMS results confirm that the mercury tris(phosphine) complexes do easily lose a phosphine ligand. It is interesting that even $[Hg(ppt)_4]^{2+}$ can be observed under ESMS conditions since this complex is so labile that it can only be observed at very low temperatures in the NMR experiment. These mass spectra testify to the very soft nature of the ion transfer from solution to gas phase.

$Hg(CF_3COO)_2$ complexes

Trifluoroacetate is a much better ligand towards mercury than perchlorate, so the formation of acetate complexes by replacement of the original anion is much less pronounced for the trifluoroacetate complexes.

The ES mass spectrum of $Hg(pom)_2(CF_3COO)_2$ (pom = tri-*o*-methoxyphenylphosphine) with B1 = 50 V shows only one significant peak at *m*/*z* 1019 due to the principal ion $[Hg(pom)_2(CF_3COO)]^+$. There are weak peaks assigned to $[Hg(pom)(CF_3COO)]^+$ (*m*/*z* 667), $[Hg(pom)(CH_3COO)]^+$ (*m*/*z* 613) and $[Hg(pom)_2]^{2+}$ (*m*/*z* 453). At a higher ion source energy (B1 = 70 V) the only significant peak is at *m*/*z* 677 due to $[Hg(pom)(CF_3COO)]^+$ suggesting that one phosphine ligand is readily lost from $[Hg(pom)_2(CF_3COO)]^+$. This was confirmed by tandem mass spectrometry; even in the absence of gas in the collision cell there was about 10% decomposition (loss of one phosphine) of selected ions of *m*/*z* 1019 showing the ion to be metastable in the gas phase. In the presence of argon in the collision cell the loss of phosphine to give $[Hg(pom)(CF_3COO)]^+$ was greatly increased.

The ES mass spectrum of $Hg(pmt)_2(CF_3COO)_2$ (pmt = tri-*m*-tolylphosphine) at low ion source energies (B1 = 40 V) shows a strong base peak at *m*/*z* 923 due to the principal ion $[Hg(pmt)_2(CF_3COO)]^+$ and a weaker peak due to $[Hg(pmt)_2(CH_3COO)]^+$ at *m*/*z* 869. At higher B1 voltages (e.g. 70 V) the ions $[Hg(pmt)(CF_3COO)]^+$ (*m*/*z* 619) and $[Hg(pmt)(CH_3COO)]^+$ are dominant. On addition of further phosphine ligand the peak due to $[Hg(pmt)_3(CF_3COO)]^+$ (*m*/*z* 1227) is observed at low ion source energies. Similar results were obtained from the ES mass spectra of $Hg(ppCl)_2(CF_3COO)_2$ (ppCl = tri-*p*-chlorophenylphosphine) and excess ligand and the data are given in Table 1.

All of the above observations are consistent with the previously reported NMR studies and it therefore seemed appropriate to extend the ESMS studies to mixed phosphine complexes of mercury. NMR experiments have previously shown that rapid exchange of phosphines occurs at mercury on the NMR timescale at room temperature, so that it is necessary to cool the solutions to low temperatures to allow the various mixed phosphine complexes to be observed by NMR spectroscopy.

Mixed phosphine complexes

The ES mass spectrum of a mixture of $Hg(pom)_2(CF_3COO)_2$ and $Hg(pmt)_2(ClO_4)_2$ shows strong peaks due to all the complexes $[Hg(pom)_2(CF_3COO)]^+$, $[Hg(pom)(pmt)(CF_3COO)]^+$ and $[Hg(pmt)_2(CF_3COO)]^+$, together with weak peaks due to the corresponding perchlorate compounds, as detailed in

TABLE 2. Electrospray mass spectra for mixtures containing two different phosphines

Mixture	Ions (m/z)
$Hg(pmt)_2(ClO_4)_2 + Hg(pom)_2(CF_3COO)_2$	$[Hg(pom)_2(CF_3COO)]^+$ (1019); $[Hg(pom)_2(ClO_4)]^+$ (1005); $[Hg(pmt)(pom)(CF_3COO)]^+$ (971); $[Hg(pmt)(pom)(ClO_4)]^+$ (957); $[Hg(pmt)_2(CF_3COO)]^+$ (923)
$Hg(pmt)_2(CF_3COO)_2 + Hg(ppCl)_2(CF_3COO)_2$	$[Hg(ppCl)_2(CF_3COO)]^+$ (1045); $[Hg(ppCl)(pmt)(CF_3COO)]^+$ (983); $[Hg(pmt)_2(CF_3COO)]^+$ (923)
$Hg(pmt)_2(CF_3COO)_2 + pmt + Hg(ppCl)_2(CF_3COO)_2 + ppCl$	$[Hg(ppCl)_3(CF_3COO)]^+$ (1411); $[Hg(ppCl)_2(pmt)(CF_3COO)]^+$ (1349); $[Hg(ppCl)(pmt)_2(CF_3COO)]^+$ (1287); $[Hg(pmt)_3(CF_3COO)]^+$ (1227)

Table 2. This mass spectrum confirms the facile exchange of phosphine ligands between mercury centres, and demonstrates the redistribution of the anionic ligands about mercury as well.

Similar exchange of phosphine ligands was observed for a mixture of $Hg(ppCl)_2(CF_3COO)_2$ and $Hg(pmt)_2(CF_3COO)_2$, for which mercury bis(phosphine) cations containing only trifluoroacetate were detected, as detailed in Table 2. When excess of the two phosphines was added to each of the compounds (to generate $Hg(phosphine)_3$ complexes) before mixing, all possible phosphine combinations of $[Hg(ppCl)_x(pmt)_{3-x}(CF_3COO)]^+$ ($x = 0$–3) were observed in the ES mass spectrum, together with the corresponding mercury bis(phosphine) compounds. Data are given in Table 2. These results confirm that rapid phosphine exchange also occurs in the mercury tris(phosphine) complexes.

Conclusions

The results presented in this paper reinforce the rapidly emerging impression that ESMS is a powerful technique for the study of speciation and equilibria in solution. Although some side reactions may occur within the ion source, the dominant peaks in the mass spectra are the principal ions pre-existing in the solution, or in the case of very labile species, daughter ions produced by collisional activation. For studies of suitable labile systems, such as these mercury systems, the combination of ESMS and multinuclear magnetic resonance studies will be particularly effective, but ESMS will also be applicable for systems not suitable for NMR studies, e.g. paramagnetic systems or those without suitable NMR nuclei. ESMS at room temperature is much more convenient than NMR spectroscopy at low temperature. In general, the only requirements are that the sample be ionic and stable in a suitable solvent (MeOH, CH_2Cl_2, CH_3CN etc.)

Experimental

Compounds were prepared as described previously [3–6].

Electrospray mass spectra were recorded by using a VG Bio-Q triple quadrupole mass spectrometer (Bio-Q, VG Bio-Tech, Altrincham, Ches., UK) with a water/methanol/acetic acid mobile phase. The compounds were dissolved in dichloromethane (2 mM) and this solution was then diluted 1:10 with methanol. The diluted solution was injected directly into the spectrometer via a Rheodyne injector using a Phoenix 20 micro LC syringe pump to deliver the solution to the vaporisation nozzle of the electrospray ion source at a flow rate of 3 μl min^{-1}. Voltages at the first skimming electrode (B1) were varied between 80 V and the minimum possible consistent with retaining a stable ion jet. This varies from time to time but is usually in the range 30–35 V. Increasing the B1 voltage enhances the formation of daughter ions by collisions with solvent molecules within the ion source. In addition, ions of a particular m/z value (e.g. the peak maximum in an isotopic mass distribution) can be selected and passed through a collision cell into a second mass analyser. In the absence of gas in the collision cell the stabilities of the selected ions can be investigated. Collision activated decomposition (CAD) mass spectra of the selected ions were obtained by admitting argon to the collision cell to a pressure that gave an approximately 50% reduction in the parent ion abundance, usually with an accelerating voltage of 200 V.

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References

1 S. O. Grim, P. J. Lui and R. L. Keiter, *Inorg. Chem., 13* (1974) 342.

2 E. C. Alyea, S. A. Dias, R. G. Goel, W. O. Ogini, P. Pilon and D. W. Meek, *Inorg. Chem., 17* (1978) 1697.

3 R. Colton and D. Dakternieks, *Aust. J. Chem., 33* (1980) 955.

4 R. Colton and D. Dakternieks, *Aust. J. Chem., 33* (1980) 1463.

5 R. Colton and D. Dakternieks, *Aust. J. Chem., 33* (1980) 1677.

6 R. Colton and D. Dakternieks, *Aust. J. Chem., 34* (1981) 323.

7 A. M. Bond, R. Colton, D. Dakternieks, M. L. Dillon, J. Hauenstein and J. E. Moir, *Aust. J. Chem., 34* (1980) 1393.

8 T. Braun and S. Zsindely, *Trends Anal. Chem., 11* (1992) 307.

9 J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong and C. M. Whitehouse, *Science, 64* (1989) 64.

10 R. D. Smith, J. A. Loo, C. G. Edmonds, C. J. Baringa and H. R. Udseth, *Anal. Chem., 62* (1990) 882.

11 R. D. Smith, J. A. Loo, R. R. Ogorzalek Loo, M. Busman and H. R. Udseth, *Mass Spectrom. Rev., 10* (1991) 359.

12 R. Colton and J. C. Traeger, *Inorg. Chim. Acta, 201* (1992) 153.

13 R. Colton, J. C. Traeger and J. Harvey, *Org. Mass Spectrom., 27* (1992) 1030.

14 R. Colton, V. Tedesco and J. C. Traeger, *Inorg. Chem., 31* (1992) 3865.

15 I. Ahmed, R. Colton, M. Jercevic, J. C. Traeger and J. N. Walter, *J. Organomet. Chem., 447* (1993) 59.

16 R. Colton, B. R. James, I. D. Potter and J. C. Traeger, *Inorg. Chem.*, accepted for publication.