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Preliminary communication

FAST ATOM BOMBARDMENT MASS SPECTROMETRY OF SOME MONO- AND POLY-NUCLEAR TRANSITION METAL COMPLEXES

REG DAVIS*, IAN F. GROVES, JAMES L.A. DURRANT,
School of Chemical and Physical Sciences, Kingston Polytechnic, Penrhyn Road, Kingston upon Thames KT1 2EE (Great Britain)
PAUL BROOKS and IVOR LEWIS
V.G. Analytical Ltd., Tudor Road, Altrincham, Cheshire, WA14 5RZ (Great Britain)

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Summary

The technique of fast atom bombardment mass spectrometry has been applied to a range of mono- and poly-nuclear transition metal complexes which do not give electron impact mass spectra. In all cases the spectra are structurally informative, although not all show molecular (M^+) or quasi-molecular ($[M + H]^+$) ions. In the cases where no M^+ or $[M + H]^+$ ions are observed, there appears to be a correlation between the ion of highest mass present and the known solution behaviour of the compound. In the case of the two cluster compounds both positive and negative ions are formed.

Mass spectrometry is now one of the standard spectroscopic methods applied to the characterisation of transition metal complexes. It is widely applied in the case of low valent, non-ionic compounds containing carbonyl and related ligands and/or organic moieties [1]. However, most spectra have been obtained using the electron impact (e.i.) method of ionisation and the requirement of volatilisation prior to ionisation by e.i. has precluded the examination of salts and covalent compounds showing low thermal stability. In some cases this method is further limited by the non-observation of molecular ions as a result of facile fragmentation and this may preclude molecular weight measurements.

These problems have, in part, been overcome by the use of the alternative ionisation techniques, chemical ionisation (c.i.) [2] and field desorption (f.d.) [3]. However, the former also requires both sample volatility and thermal

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*Author to whom correspondence should be addressed.

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stability and the latter suffers from the fact that in many cases the ion produced are particularly transitory, sometimes lasting only a few seconds [4].

The recently described fast atom bombardment (FAB) method of ionisation has been shown to have the potential for overcoming all these problems. It is a relatively soft method of ionisation when compared to e.i., but usually provides some fragmentation data. It does not require sample volatilisation and ion beams are persistent [4]. Relatively few reports of FAB mass spectra of metal-containing compounds (except Group I metal salts of organic acids) have been published [4,5] and none of those so far examined are salts or polynuclear metal containing compounds.

We have, therefore, applied the FAB technique to the compounds listed in Table 1, which were chosen for the following reasons. Obtaining mass spectra of molecules containing triarylphosphane and related ligands has been a long-

TABLE 1

FAB MASS SPECTRA OF SOME INORGANIC COMPOUNDS [a]

I	$[\mathrm{RhCl(PPh_3)_3}]$ [b] (dap and MeCN), 925, 1.5, $(M+\mathrm{H})^+$; 924, 1.0, $M^{+\cdot}$; 890, 20.5, $(M+\mathrm{H}-\mathrm{Cl})^{+\cdot}$; 889, 28.8, $(M-\mathrm{Cl})^+$; 663, 11.0, $(M+\mathrm{H}-\mathrm{PPh_3})^+$; 662, 27.4, $(M-\mathrm{PPh_3})^{+\cdot}$; 628, 41.4, $(M+\mathrm{H}-\mathrm{PPh_3}-\mathrm{Cl})^{+\cdot}$; 627, 100.0, $(M-\mathrm{PPh_3}-\mathrm{Cl})^+$; 551, 11.0, $(M+\mathrm{H}-\mathrm{PPh_3}-\mathrm{Cl}-\mathrm{Ph})^+$; 550, 27.4, $(M-\mathrm{PPh_3}-\mathrm{Cl}-\mathrm{Ph})^{+\cdot}$
II	$[\mathrm{RhBr(PPh_3)_3}]$ [c] (dap and MeCN), 969, 0.5, $(M+\mathrm{H})^+$; 968, 0.6, $M^{+\cdot}$; 890, 13.6, $(M+\mathrm{H}-\mathrm{Br})^{+\cdot}$; 889, 18.2, $(M-\mathrm{Br})^+$; 707, 22.7, $(M+\mathrm{H}-\mathrm{PPh_3})^+$; 706, 59.0, $(M-\mathrm{PPh_3})^{+\cdot}$; 628, 43.2, $(M+\mathrm{H}-\mathrm{PPh_3}-\mathrm{Br})^{+\cdot}$; 627, 100.0, $(M-\mathrm{PPh_3}-\mathrm{Br})^+$
III	$[\mathrm{RuCl_2(PPh_3)_3}]$ [d] (dap and MeCN), 697, 22.2, $(M+\mathrm{H}-\mathrm{PPh_3})^{+\cdot}$; 696, 33.3, $(M-\mathrm{PPh_3})^{+\cdot}$; 662, 26.7, $(M+\mathrm{H}-\mathrm{PPh_3}-\mathrm{Cl})^{+\cdot}$; 661, 40.0, $(M-\mathrm{PPh_3}-\mathrm{Cl})^+$; 627, 62.2, $(M+\mathrm{H}-\mathrm{PPh_3}-2\mathrm{Cl})^{+\cdot}$; 626, 68.9, $(M-\mathrm{PPh_3}-2\mathrm{Cl})^{+\cdot}$; 365, 53.3, $(M+\mathrm{H}-2\mathrm{PPh_3}-2\mathrm{Cl})^{+\cdot}$; 364, 40.0, $(M-2\mathrm{PPh_3}-2\mathrm{Cl})^{+\cdot}$; 363, 100, $(M-2\mathrm{PPh_3}-2\mathrm{Cl}-2\mathrm{H})^{+\cdot}$
IV	$[\mathrm{ReCl(CO)_3}\{\mathrm{P((C_6H_4F}\text{-}p)_3\}_2]$ [e] (dap; gly), 902, 42.0, $(M+\mathrm{H}-\mathrm{Cl})^{+\cdot}$; 901, 100.0, $(M-\mathrm{Cl})^+$; 87.4, 23.7, $(M+\mathrm{H}-\mathrm{Cl}-\mathrm{CO})$; 873, 55.3, $(M-\mathrm{Cl}-\mathrm{CO})^+$
V	$[\mathrm{Re(ONO_2)(CO)_3}\{\mathrm{P(C_6H_4Me}\text{-}p)_3\}_2]$ [f] (dap; gly), 878, 59.1, $(M+\mathrm{H}-\mathrm{NO_3})^+$; 877, 100.0, $(M-\mathrm{NO_3})^+$; 850, 21.1, $(M+\mathrm{H}-\mathrm{NO_3}-\mathrm{CO})^{+\cdot}$; 849, 43.7, $(M-\mathrm{NO_3}-\mathrm{CO})^+$; 573, 9.9, $(M-\mathrm{NO_3}-\mathrm{P(C_6H_4Me)_3})$
VI	$[\mathrm{Pd(PPh_3)_4}]$ [g] (dap; gly), 892, 12.6, $(M-\mathrm{PPh_3})^{+\cdot}$; 891, 12.6, $(M-\mathrm{PPh_3}-\mathrm{H})^+$; 630, 100.0, $(M-2\mathrm{PPh_3})^{+\cdot}$; 629, 26.3, $(M-2\mathrm{PPh_3}-\mathrm{H})^+$; 368, 36.8, $(M-3\mathrm{PPh_3})^{+\cdot}$
VII	$[\mathrm{Pt(PPh_3)_4}]$ [h] (gly), 1438, 1.8, $\{\mathrm{Pt_2(PPh_3)_4}\}^{+\cdot}$; 1361, 3.0, $\{\mathrm{Pt_2(PPh_3)_3(PPh_2)}\}^+$; 1284, 2.3, $\{\mathrm{Pt_2(PPh_3)_2(PPh_2)_2}\}^{+\cdot}$; 1176, 2.8, $\{\mathrm{Pt_2(PPh_3)_3}\}^{+\cdot}$; 1099, 39, $\{\mathrm{Pt_2(PPh_3)_2(PPh_2)}\}^+$; 981, 21.4, $(M-\mathrm{PPh_3})^{+\cdot}$; 914, 4.5, $\{\mathrm{Pt_2(PPh_3)_2}\}^{+\cdot}$; 719, 100.0, $(M-2\mathrm{PPh_3})^{+\cdot}$; 457, 53.1 $(M-3\mathrm{PPh_3})^{+\cdot}$
VIII	$[\mathrm{Fe_4(H)C(CO)_{12}AuPPh_3}]$ [i] (carb), Positive ion: 1033, 60, $(M+\mathrm{H})^+$; 1005, 60, $(M+\mathrm{H}-\mathrm{CO})^+$; 949, 100, $(M+\mathrm{H}-2\mathrm{CO})^+$. Negative ion: 1033, 8.2, $(M+\mathrm{H})^{-\cdot}$; 1032, 7.3, $M^{-\cdot}$; 1005, 25.5, $(M+\mathrm{H}-\mathrm{CO})^-$; 1004, 8.2, $(M-\mathrm{CO})^{-\cdot}$; 893, 13.2, $(M+\mathrm{H}-5\mathrm{CO})^-$
IX	$[\mathrm{Os_4H_3(CO)_{12}(CH_3CN)_2}](\mathrm{PF_6})$ [j], (carb.), Positive ion: 1189, 389, C^+; 1107, 100.0, $(C-2\mathrm{CH_3CN})^+$; 1077, 52.8, $(C-2\mathrm{CH_3CN}-2\mathrm{H}-\mathrm{CO})^+$; 1049, 47.2, $(C-2\mathrm{CH_3CN}-2\mathrm{H}-2\mathrm{CO})^+$. Negative ion: 1107, 100.0, $(C-2\mathrm{CH_3CN})^-$; 1079, 66.7; $(C-2\mathrm{CH_3CN}-\mathrm{CO})^-$; 1049, 53.3, $(C-2\mathrm{CH_3CN}-2\mathrm{CO}-2\mathrm{H})^-$; 1020, 23.3, $(C-2\mathrm{CH_3CN}-3\mathrm{CO}-3\mathrm{H})^-$; 992, 36.7, $(C-2\mathrm{CH_3CN}-4\mathrm{CO}-3\mathrm{H})^-$; 964, 25.0, $(C-2\mathrm{CH_3CN}-5\mathrm{CO}-3\mathrm{H})^-$

[a] Recorded on a VG ZAB using xenon bombardment. Matrix materials are dap = diamylphenol, gly = glycerol, carb = carbowax 200. In the cases of I–III a small amount of MeCN was added to aid solubility. *m/z*, relative abundance and assignment listed. [b] Based on ^{35}Cl, ^{103}Rh. [c] Based on ^{79}Br, ^{103}Rh. [d] Based on ^{35}Cl, ^{102}Ru. [e] Based on ^{35}Cl, ^{185}Re. [f] Based on ^{185}Re. [g] Based on ^{106}Pd, $[M-\mathrm{PPh_3}]^{+\cdot}$ not observed in the spectrum recorded from dap. [h] Based on ^{195}Pt. [i] Based on ^{56}Fe, ^{197}Au. [j] Based on ^{192}Os, C = cation.

standing problem. For example, the e.i. mass spectra of compounds I, III and VII consist only of ions arising from Ph_3P, which is produced as a result of thermal decomposition of the complexes. It would therefore be extremely useful if FAB mass spectrometry could be used in the characterisation of such compounds. Compound VIII is a heteropolynuclear complex also containing PPh_3 and compound IX is a salt containing a polynuclear cation. Neither of these compounds yield e.i. mass spectra.

Table 1 lists the complexes examined, the matrices used on the FAB probe, and the mass/charge ratios and relative intensities of the principal ions observed in each case. The technique is exemplified by the spectrum of $[RhCl(PPh_3)_3]$ (I). Although of low intensity, the molecular ion is clearly discernible and an adequate number of fragment ions are observed. II shows a similar spectrum, although the relative intensity of the molecular ion is reduced.

The spectrum of III shows $[(M + H) - PPh_3]^{+\cdot}$ as its highest mass ion. Although this is disappointing from the point of view of compound characterisation, it is consistent with the known solution behaviour of this molecule [6] and although the details of the FAB ionisation process are at present only sketchily understood, solubility and/or dispersion in the matrix are known to be of major importance [4].

IV and V both show $[(M + H) - X]^+$ (IV, X = Cl; V, $X = NO_3$) as their highest mass ions. There is no published evidence that these molecules undergo dissociation into $[Re(CO)_3\{PR_3\}_2]^+$ and X^- ions in solution, although behaviour of this type has been noted for $[M(ONO_2)(CO_5)]$ (M = Mn, Re) [7]. In the compounds under examination here the missing molecular ions may arise as a result of facile Re—X bond cleavage after ionisation.

VI and VII are, however, known to undergo extensive dissociation in solution, giving $[M(PPh_3)_3]$ [8]. In accord with this VI shows $[Pd(PPh_3)_3]^{+\cdot}$ as the highest mass ion in the spectrum obtained from a glycerol matrix. Fragment ions corresponding to $[Pd(PPh_3)_n]^{+\cdot}$ (n = 2, 1) are also observed. However, the spectrum recorded from diamylphenol shows no ions of mass higher than that of $[Pd(PPh_3)_2]^{+\cdot}$. Similarly, VII shows $[Pt(PPh_3)_n]^{+\cdot}$ (n = 3—1) when recorded from glycerol, but unlike VI, also shows the dinuclear species $[Pt_2(PPh_3)_n]^{+\cdot}$ (n = 4—2) in low abundance. Unusually both VI and VII show ions derived from $M^{+\cdot}$ rather than from the quasi-molecular ion, $[M + H]^+$. Such behaviour has also been noted for $[Rh(1,5\text{-}COD)\{C_5H_4(CH_2)_3Si(OMe)_3\}]$ [5(a)].

None of the compounds I—VII show negative ion spectra.

The cluster compound VIII showed quasi-molecular ions $[M + H]$ in both positive and negative ion spectra. The signal to noise ratio appears to be better in the negative ion spectrum, but this arises as a consequence of a weaker matrix spectrum in this mode as has been previously observed [4]. The observation of $[M + H]^-$ is unexpected as previous studies on organic molecules have shown $[M - H]^-$ ions are typically observed. The fragmentation differs slightly in the two ionisation modes as has been observed in the positive and negative spectra of trinuclear clusters using e.i. ionisation [9].

The salt, IX, containing a cluster cation, also exhibits both positive and negative ion spectra. The former gives $[Os_4H_3(CO)_{12}(CH_3CN)_2]^+$ as its highest mass ion; however, the most intense ion is $[Os_4H_3(CO)_{12}]^+$. In the negative ion spectrum $[Os_4H_3(CO)_{12}(CH_3CN)_2]^-$ is not observed, but $[Os_4H_3(CO)_{12}]^-$ and fragment ions arising via loss of CO and H ligands are clearly visible. It is relevant that quantitative electrochemical reduction of $[Os_4H_3(CO)_{12}(CH_3CN)_2]^+$ to $[Os_4H_3(CO)_{12}]^-$ has been reported [10]. Neither positive or negative ion spectra of IX display ions corresponding to (cation + anion). The use of a mass spectrometer of reverse geometry precludes the observation of normal metastable ions in this study; however, that such ions are formed is confirmed by a MIKES scan on the ion $[Rh(PPh_3)_3]^+$ in the spectrum of I. This showed an ion at *m/z* 627 arising from loss of PPh_3.

For all compounds examined in this work, the spectra were reasonably persistent, lasting at least five minutes in each case.

We believe this study has demonstrated the potential of FAB mass spectrometry for transition metal complexes and predict that the method will become an important weapon in the inorganic and organometallic chemists' spectroscopic arsenal.

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