Field Desorption Mass Spectrometry: a Novel Method for the Characterisation of Cationic Co-ordination Complexes

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Summary Field desorption (F.D.) mass spectrometry has been shown to provide a novel and easy method for the characterisation of salts of monocationic metal complexes; in most cases the base peaks correspond to the molecular ion for the cation and no fragmentation is observed, but with *trans*-$[Co(en)_2Cl_2]Cl$ (en = ethylenediamine) and some related *trans*-complexes one amine ligand is lost in the base peak, and further loss of a halide ligand is observed.

The involatile nature of co-ordination complex salts has to date precluded their characterisation by conventional electron impact (E.I.) and chemical ionization (C.I.) mass spectrometry. Following our recent success in obtaining field desorption (F.D.) mass spectra with organometallic salts,[1] we now report the results of similar studies with salts of classical (Werner-type) co-ordination complexes.

Solutions of the co-ordination complexes were prepared in methanol, methanol–water, or Me_2SO, and evaporated on to conventional activated carbon emitters. Their F.D. mass spectra were recorded with a Varian combined F.D.–F.I.–E.I. source on a CH5D mass spectrometer linked to a Varian 620 i data system. Emitter heating currents in the range 8–12 mA were sufficient to desorb the complex cations.

The majority of monocationic metal complexes investigated to date showed extremely simple F.D. mass spectra. Thus, for the compounds [Pd(dien)X]X [X = Cl or I; dien = iminobis(ethyleneamine)], $[Pd(Et_4dien)X]X$ [X = I or NCS; Et_4dien = iminobis(ethylenediethylamine)], *cis*-$[Co(en)_2X_2]Y$ ($X = NO_2$, Y = I; or X = NCS, $Y = NO_3$; en = ethylenediamine), $[Co(en)_2(salicylato)]NO_3$, and *cis*-$[Ru(en)_2Cl_2]Cl{\cdot}H_2O$, the base peaks corresponded to the molecular ions M^+ for the respective cations. The only other significant peaks were those expected for the various metal and ligand isotopes. No fragmentation products were observed.

With the [Pd(Et_4dien)X]X (X = Cl or NCS) complexes, ions corresponding to the cluster species {[Pd(Et_4dien)X]X [Pd(Et_4dien)X]}$^+$ were also observed, allowing the additional identification of the anion.

However, for the related monocationic complexes *trans*-[Co(en)$_2$X$_2$]X (X = Cl or Br) and *trans*-[Co{(−)-pn}$_2$-Cl$_2$]Cl (pn = 1,2-diaminopropane), the F.D. mass spectra were more complicated. No M^+ peaks were observed. Instead, each of these compounds gave a base peak corresponding to the loss of one amine ligand from the cation molecular ion. In addition, with *trans*-[Co(en)$_2$Cl$_2$]Cl and *trans*-[Co{(−)-pn}$_2$Cl$_2$]Cl loss of one chloride ligand gave rise to further fragment ions. It may be significant that this more complex behaviour has so far only been observed in complexes with a *trans*-geometry.

The above results indicate that F.D. mass spectrometry provides a novel and easy technique for the characterization of monocationic co-ordination complexes. It may also assist in the correct formulation of potentially ambiguous species. For example, covalent hydrates such as [ML$_2$-(LH$_2$O)]$^{n+}$ (L = *N*-heterocycle) should be readily distinguished from related [ML$_3$]$^{n+}$ cations containing water of crystallisation.

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[1] D. E. Games, A. H. Jackson, L. A. P. Kane-Maguire, and K. Taylor, *J. Organometallic Chem.*, 1975, **88**, 345.