Characterisation of Cationic Co-ordination Complexes using Field Desorption Mass Spectrometry

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Field desorption (f.d.) mass spectrometry has been shown to provide a useful method for the characterisation of involatile monocationic co-ordination complexes. With square-planar compounds of the type [Pd(dien)X]X [X = Cl or Br; dien = iminobis(ethyleneamine)], [Pd(Et$_4$dien)X]X [X = I or NCS; Et$_4$dien = iminobis(ethylenediethylamine)], and a variety of octahedral complexes of the type *cis*-[Co(en)$_2$X$_2$]Y (X = NO$_2$, Y = I; or X = NCS, Y = NO$_3$; en = 1,2-diaminoethane), [Co(en)$_2$(sal)][NO$_3$] (sal = salicylate), and *cis*-[Ru(en)$_2$Cl$_2$]Cl the base peak corresponds to the molecular ion $[M]^{\cdot +}$ for the cation and no fragmentation is observed. However, for the related complexes *trans*-[Co(en)$_2$X$_2$]X (X = Cl or Br) and *trans*-[Co{(−)pn}$_2$Cl$_2$]Cl (pn = 1,2-diaminopropane) no $[M]^{\cdot +}$ peaks are observed, and fragment ions associated with ligand loss are seen. Useful f.d. mass spectra can also be obtained with some di- and tri-cationic co-ordination complexes, but the results are less reproducible and sometimes difficult to rationalise.

ELECTRON impact (e.i.) and chemical ionisation (c.i.) mass spectrometry have been widely employed for the rapid characterisation of volatile organic and organometallic compounds. Studies have also appeared[1] on the mass spectral (e.i.) behaviour of limited classes of volatile neutral co-ordination complexes such as metal acetylacetonates.[2] However, the involatile nature of the vast majority of co-ordination complexes has to date generally precluded their characterisation by conventional mass spectrometry. Particularly intractable in this respect have been the very extensive range of co-ordination complex salts.

Since field desorption (f.d.) mass spectrometry does not require the prior volatilisation of the sample, we have investigated the potential of this technique for the characterisation of cationic co-ordination complexes. This method has recently been shown to be of considerable value in the study of both cationic[3-5] and neutral[6-8] organometallic complexes, where the base peaks in the f.d. mass spectra generally corresponded to the molecular ions associated with the cationic portion of the complexes. Some limited studies have also been reported on classical co-ordination complexes, including crown ether[9,10] and cryptate[11] complexes, as well as anionic species.[12] In the present study a wide range of monocationic co-ordination complexes are investigated (of square-planar or octahedral geometry), together with a limited number of di- and tri-cationic species. A preliminary report has appeared.[13]

EXPERIMENTAL

Analytically pure samples of the various complexes were available from other studies in our laboratories. Solutions of the desired complexes were prepared in methanol, methanol–water, water, or dimethyl sulphoxide (dmso), and evaporated onto 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 SS100i data system. Emitter heating currents in the range 8—12 mA were sufficient to desorb each of the cations.

RESULTS AND DISCUSSION

Typical f.d. mass spectra for a range of monocationic co-ordination complexes are collected in Table 1, while results for di- and tri-cationic species (together with some neutral complexes) are summarised in Table 2.

Each of the monocationic square-planar palladium(II) complexes in Table 1 gave good f.d. mass spectra. For

TABLE 1

f.d. mass spectra of monocationic co-ordination complexes

Complex	Solvent	Emitter current/mA	*m*/*z* (% relative abundance)
[Pd(dien)Cl]Cl	Methanol	12	250(8), 249(3), 248(10), 247(12), 246(100), 245(15), 244(38), 242(26)
[Pd(dien)I]I	Methanol	11	340(18), 339(2), 338(68), 337(7), 336(100), 335(56), 334(26)
[Pd(Et$_4$dien)Cl]Cl	Methanol	10	756(2), 755(3), 754(5), 752(18), 751(10), 750(8), 749(10), 748(10), 747(7), 746(5), 745(1), 744(1), 742(1), 395(1), 392(2), 391(4), 390(2), 389(1), 363(1), 362(4), 361(9), 360(26), 359(39), 358(56), 357(86), 356(63), 355(100), 354(63), 353(35), 352(3), 351(2)
[Pd(Et$_4$dien)(NCS)][NCS]	Methanol	10	825(6), 819(6), 817(9), 815(4), 385(27), 384(19), 383(100), 382(92), 381(46), 380(5), 379(45) 378(8), 377(5)
cis-[Co(en)$_2$(NO$_2$)$_2$]I	dmso	8	273(1), 272(77), 271(100)
[Co(en)$_2$(NCS)$_2$][NO$_3$]	Methanol	10	299(8), 298(1), 297(9), 296(11), 295(100)
[Co(en)$_2$(sal)][NO$_3$]	Methanol	9	317(1), 316(8), 315(100)
trans-[Co(en)$_2$Cl$_2$]Cl	Methanol	8	347(4), 346(4), 345(12), 343(3), 216(1), 214(3), 194(1), 193(10), 192(4), 191(69), 190(8), 189(100), 156(2), 154(13)
trans-[Co{(−)pn}$_2$Cl$_2$]Cl	Methanol	12	207(7), 206(4), 205(57), 204(4), 203(100), 170(3), 168(6)
trans-[Co(en)$_2$Br$_2$]Br	dmso	8	478(3), 477(8), 476(4), 281(53), 280(8), 279(100), 278(3), 277(68)
cis-[Ru(en)$_2$Cl$_2$]Cl·H$_2$O	Water–methanol	8	296(17), 295(4), 294(100), 293(17), 292(82), 291(44), 290(29), 289(16), 288(9), 286(9)

TABLE 2

f.d. mass spectra of di- and tri-cationic and neutral co-ordination complexes

Complex	Solvent	Emitter current/mA	m/z (% relative abundance)
$[Ru(nphen)_3][NO_3]_2$	Water	10	391(8), 390(19), 389.5(38), 389(21), 388.5(100), 387.5(69), 387(76), 386.5(10), 386(2), 385.5(7), 385(8), 381(3), 380(3), 194(9), 193(22)
cis-$[Co(trien)Cl(OH_2)]Cl_2$	Water	8	515(7), 278(5), 277(27), 275(30), 242(27), 241(11), 240(100)
$[Co(NH_3)_5Cl]Cl_2$	Water	12	131(43), 130(7), 129(100)
$[Co(en)_3]I_3$	dmso	9	621(2), 620(11), 374(3), 373(100), 247(1), 246(23)
$[VO(acac)_2]$	Acetone	10	267(3), 266(5), 265(100), 215(4), 214(29)
$[Cu(pyca)_2]\cdot 2H_2O$ *	Water	8	311(3), 310(10), 309(58), 308(14), 307(100), 265(2), 263(5)

* pyca = Pyridine-2-carboxylate.

example, the base peak for the complex $[Pd(dien)Cl]Cl$ [dien = iminobis(ethyleneamine)] corresponded to the molecular ion, $[M]^{\cdot +}$, for the cation at m/z 246 ($^{108}Pd^{35}Cl$). No fragment ions were observed, the only other significant peaks being those expected for the various palladium and chlorine isotopes. The desorption process was smooth and several spectra could be obtained from each emitter loading. Simple spectra were also obtained for the salt $[Pd(dien)I]I$, the base peak being the cationic molecular ion at m/z 336 (^{106}Pd).

The related palladium(II) complexes $[Pd(Et_4dien)X]X$ [X = Cl or NCS; Et_4dien = iminobis(ethylenediethylamine)] also exhibited base peaks corresponding to the cationic molecular $[M]^{\cdot +}$ ions at m/z 355 and 383 respectively. Interestingly, for the former complex an isotopic spread of weak peaks centred at m/z 390 indicated the presence of ions corresponding to the whole complex, *i.e.* $[M^+Cl^-]^+$. However, the strongest evidence for the nature of the counter anions in these two complexes was the presence in both cases of cluster ions of the type $[\{Pd(Et_4dien)X\}_2X]^+$, centred at m/z 752 and 817 respectively. Again no fragmentations were observed. These series of square-planar palladium(II) complexes indicate that for such salts f.d. mass spectrometry provides a ready means of molecular-weight determination for the cation and in some cases for the anion as well.

Several of the monocationic octahedral complexes in Table 1 also yielded very simple f.d. mass spectra. Thus, for the compounds *cis*-$[Co(en)_2X_2]Y$ ($X = NO_2$, $Y = I$; $X = NCS$, $Y = NO_3$; en = 1,2-diaminoethane), *cis*-$[Co(en)_2(sal)][NO_3]$ (sal = salicylate), and *cis*-$[Ru(en)_2Cl_2]Cl\cdot H_2O$, the base peaks again corresponded to the molecular ions $[M]^{\cdot +}$ for the respective cations (at m/z 271, 295, 315, and 294 respectively). The only other ions observed were those expected for the various metal and ligand isotopes. In the case of the ruthenium(III) complex it should be noted that the base peak at m/z 294 represents a combination of the two species $[^{102}Ru(en)_2{}^{35}Cl^{37}Cl]^+$ and $[^{104}Ru(en)_2{}^{35}Cl_2]^+$, resulting in it being more intense than the expected cation molecular ion at m/z 292, $[^{102}Ru(en)_2{}^{35}Cl_2]^+$. No cluster ions were noted for any of these complexes, precluding any information on the anionic portion of the molecule.

However, the related monocationic octahedral complexes *trans*-$[Co(en)_2X_2]X$ (X = Cl or Br) and *trans*-$[Co\{(-)pn\}_2Cl_2]Cl$ (pn = 1,2-diaminopropane) revealed more complicated f.d. mass spectra. No molecular $[M]^{\cdot +}$ ions corresponding to the cationic portion of the molecules were found. Instead, each of the complexes showed a base peak corresponding to the loss of one amine ligand from the cation, *i.e.* $[M - \text{amine}]^+$. No further fragmentation was observed for *trans*-$[Co(en)_2Br_2]Br$. However, with *trans*-$[Co(en)_2Cl_2]Cl$ and *trans*-$[Co\{(-)pn\}_2Cl_2]Cl$ peaks were also found at m/z 156, 154 and 170, 168 respectively, due to the fragment ions $[M - \text{amine} - Cl]^+$. In addition, *trans*-$[Co(en)_2Cl_2]Cl$ also exhibited weak peaks at m/z 216 and 214 arising from loss of a chloride ligand from the cation molecular ion. However, in each of these three last mentioned complexes amine loss is obviously the dominant fragmentation pathway.

Another interesting feature of the f.d. mass spectra of the salts *trans*-$[Co(en)_2X_2]X$ (X = Cl or Br) was the presence of significant peaks at m/z 345 and 477 respectively. These could be due to unusual gas-phase polymeric species of the type $[Co_2(en)_2X_3]^+$. However, they are more probably associated with the cluster ions $[(M - \text{amine} - X)_2X]^+$.

The f.d. mass spectrometric behaviour of a limited number of di- and tri-cationic metal complexes has also been investigated. The results to date suggest that they generally give more complex f.d. mass spectra than related monocationic species. Spectra were less reproducible and were sometimes difficult to rationalise with the expected structures. For example, $[Co(NH_3)_5Cl]Cl_2$ did not exhibit a peak for the expected cation molecular ion, but showed peaks at m/z 131, 130, and 129 (base peak) which may be assigned to the species $[CoCl_2]^+$. Desorption of this complex is apparently accompanied by extensive fragmentation.

However, sensible f.d. mass spectra were obtained for the dicationic complexes $[Ru(nphen)_3][NO_3]_2$ (nphen = 5-nitro-1,10-phenanthroline) and *cis*-$[Co(trien)Cl(OH_2)]Cl_2$ (trien = triethylenetetramine) (Table 2). The base peak at m/z 388.5 for the former complex corresponds to the doubly charged cation molecular ion $[M]^{2+}$ (^{102}Ru). Most of the other peaks arise from the other ruthenium isotopes. Protonated $[M + 1]^{2+}$, $[M + 2]^{2+}$, and $[M + 3]^{2+}$ species are also apparent (*e.g.* the peaks at m/z 391 and 390), a feature common in the f.d. mass spectra of organic molecules. Very little fragmentation was noted, the only other significant peaks being two of unknown origin at m/z 194 and 193.

In contrast, the base peak for *cis*-$[Co(trien)Cl(OH_2)]Cl_2$ at m/z 240 corresponds to the singly charged ion $[M - H_2O]^+$, arising from loss of a co-ordinated water molecule from the complex cation. Analogous loss of solvate in the f.d. mass spectra of organometallic complexes [6] and of co-ordinated water from crown ether complexes of alkali metals [10] has been previously noted. No other fragmentation was observed. However, a weak peak was found at m/z 515 which may be assigned to the cluster ion $[(M - H_2O)_2Cl]^+$, confirming the nature of the counter anion. Interestingly, an unexpected feature of this particular spectrum was the presence of moderately intense peaks at m/z 277 and 275 which are undoubtedly due to the dichloro-monocation $[Co(trien)Cl_2]^+$. These may arise from the solid-state conversion of the original complex *cis*-$[Co(trien)Cl(OH_2)]Cl_2$ to *cis*-$[Co(trien)Cl_2]Cl{\cdot}H_2O$ during long-term storage. A more probable explanation is anation displacement of the co-ordinated water by a chloride counter anion in the concentrated aqueous solution present during the final stages of sample evaporation onto the emitter wire. Alternatively, the $[Co(trien)Cl_2]^+$ ion may be formed during desorption or arise from some gas-phase process in the mass spectrometer. The use of a non-co-ordinating counter anion such as the $[BF_4]^-$ ion should help to resolve this question.

The only tricationic complex investigated to date, namely $[Co(en)_3]I_3$, also gave an unusual f.d. mass spectrum (Table 2). The base peak at m/z 373 can be assigned to the species $[Co(en)_2I_2]^+$. The inertness of the initial $[Co(en)_3]^{3+}$ cation to nucleophilic attack by iodide ions in solution precludes the formation of this di-iodobis(1,2-diaminoethane) species during deposition onto the emitter wire. The fragment ion $[Co(en)I_2]^+$ was also observed at m/z 246. Interestingly, a further peak was also noted at m/z 620, corresponding to both the anion and cation, *i.e.* $[Co(en)_3I_3]^+$. At present, we can offer no rationale for the above behaviour of $[Co(en)_3]I_3$ in the f.d. mass spectrometer.

Finally, included in Table 2 are the f.d. mass spectra of two neutral co-ordination complexes. Electron impact (e.i.) mass spectral data have been previously reported for the relatively volatile vanadyl complex $[VO(acac)_2]$ (Hacac = acetylacetone), showing a base peak molecular ion and a very intense $[M - acac]^+$ fragmentation. Several other fragment ions were observed [2] in the e.i. mass spectrum, including $[VO(acac)_2 - CH_3]^+$, $[VO(acac)(OH)]^+$, and $[V]^+$. The f.d. mass spectrum of this vanadyl complex also exhibited a molecular ion at m/z 265 as base peak. However, in contrast to the e.i. results, very little fragmentation was observed. This difference in complexity between the f.d. and e.i. mass spectra of volatile compounds has been previously noted for neutral organic [14] and organometallic [6] species. The complex bis(pyridine-2-carboxylato)copper(II) also gave a f.d. mass spectrum with a base peak molecular ion (m/z 307). The only fragment ion observed was at m/z 263, which corresponds to loss of carbon dioxide from the molecular ion.

The above results indicate that f.d. mass spectrometry provides a useful method for the characterisation of monocationic co-ordination complexes. It is, however, still to be established why some octahedral complexes do not exhibit molecular $[M]^{\cdot +}$ ions. In this respect, it may be significant that all of the octahedral cations examined to date which show ligand loss in their base peaks have a *trans* geometry. Finally, while f.d. mass spectrometry can give useful information on di- and tri-cationic complexes, further studies are necessary to determine the reliability of the technique for these more highly charged species.

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