PART II
CHAPTER I

INTRODUCTION

In the last few decades mass spectrometry has undergone remarkable growth and has become a technique of great utility in chemistry. Earlier, mass spectrometric studies were carried out only for organic compounds. But during the last two decades its application has been extended to inorganic compounds also\textsuperscript{243,244}.

In general, a mass spectrometer will have three basic components. They are

a) the ion source where the gaseous ions are produced,
b) the mass analyser where the ions are separated, and
c) the detector where the separated ions are detected and their intensities measured.

Thus, in a mass spectrometer ions are produced from a molecule vapourised in high vacuum, then separated according to their mass to charge ratio and finally recorded. For details of instrumentation and presentation of mass spectra, various references are available\textsuperscript{245,246}.

The main applications of mass spectrometry in studies of metal compounds are

a) molecular mass and molecular formula determination,
b) determination of structure by analysis of fragmentation
patterns,
c) quantitative analysis of metals, and
d) determination of appearance and ionisation potentials.

General features of fragmentation of metal containing ions

Generally the method of fragmentation of an ion depends on
a) the ionisation potential and relative stabilities of the possible fragment species,
b) the relative stabilities of the bonds and
c) the possibility of breaking down through rearrangement processes involving a cyclic transition state\(^{245}\).

The most abundant ions in a mass spectrum correspond to ions, which are stable and are products of most favourable fragmentation path. In the case of metal containing ions the nature of the metal and the number and relative stabilities of the oxidation states of the metal influence the fragmentation pattern of the metal containing ion. Stevenson proposed a useful rule for the fragmentation behaviour of alkanes\(^ {247}\). It is found that the positive charge remained with the more highly substituted fragment, that is, the one with lower ionisation potential. Therefore it was concluded that when an ion fragments, the positive charge will remain on the fragment of lower ionisation
potential. The ionisation potential of metal containing fragments are almost always lower than the ionisation potentials of the respective ligands. Therefore, when a metal containing ion fragments, the charge will most probably remain with the metal containing fragment.

\[
ML_n^+ \rightarrow ML_{n-1}^+ + L
\]

Stability of a species depends on whether it is an odd or even electron species. It is reasonable to assume that even electron species are, in general, more stable than odd electron species. Odd electron ions, both molecular and fragment are designated by the superscript +. This symbol indicates both the ionic and radical character of the species. Even electron ions are designated by the superscript symbol +.

In the case of metal compounds, the nature of odd and even electron species has been studied in detail\(^{248,249}\). For transition metal compounds the situation is not analogous to that of organic compounds. This is because some of the compounds of transition metals will contain an even number of electrons which may not be fully paired. Consequently, in such compounds, the relationship between a molecule and its molecular ion, in terms of odd and even electron considerations is not always analogous to that of
organic compounds.

To decide whether a species is odd or even electron, the non-bonding electrons of the central metal are usually excluded from electron counting. These electrons are considered only when a change in oxidation state of the metal occurs. Therefore the metal containing molecule will almost always be an even-electron species in mass spectrometric terms, irrespective of the oxidation number and spin multiplicity of the metal.

The probable modes of fragmentation of odd and even electron ions are as follows

\[ \text{O}^+ \xrightarrow{\text{---}} \text{P}^+ + \text{radical} \]
\[ \text{O}^+ \xrightarrow{\text{-->}} \text{Q}^+ + \text{EES} \]
\[ \text{E}^+ \xrightarrow{\text{---}} \text{R}^+ + \text{EES} \]
\[ \text{E}^+ \xrightarrow{\text{-->}} \text{S}^+ + \text{radical} \]

EES = even electron species

For organic compounds it is found that odd electron ions decompose by both pathways; but even electron ions decompose mainly by losing an even electron species. On the contrary in metal compounds, loss of a radical from an
even electron species is frequently observed.

In terms of odd and even electron considerations, metal compounds can be classified as follows
(a) Compounds where the ligand is essentially $\sigma$-bonded to the metal
(b) $\pi$-bonded complexes of the transition metals

The molecular ion of the former fragments mainly by radical elimination. The fragmentation of $\pi$-bonded transition metal complexes is through elimination of an even electron species. This will be so if the ionisation of molecule involves removal of an electron from a bonding orbital in case of (a), but from a non-bonding orbital in the case of (b). Thus, molecular ions of (a) are odd electron ions while that of (b) are even electron ions.

FRAGMENTATION PATTERNS OF $\sigma$-BONDED COMPOUNDS

A hypothetical $\sigma$-bonded compound $\text{ML}_n$ may be considered to discuss the generalised fragmentation patterns. The decomposition of molecular ions of the type $\text{ML}_n^+$ generally involves radical elimination. Thus an even electron ion is produced. The metal-ligand bond or some bonds in the ligand can be cleaved for the elimination of a radical.

The elimination of the radical from the molecular
ion $ML^+$ and the possible modes of decomposition of the even electron ion formed are given in scheme 1.

\[ ML^{++} \]

- radical

\[ (L-a) ML_n^{-1} \]

- radical

\[ ML_n^{-2} \]

- radical

\[ ML_n^{-1} \]

- radical

\[ L \]

\[ EENS \]

\[ OEI \]

\[ EEI \]

\[ EENS \]

\[ OEI \]

\[ ML_n^{-2} \]

\[ EEI \]

\[ EENS \]

EENS = even electron neutral species
EEI = even electron ion
OEI = odd electron ion

The decomposition of the even electron ions $ML_n^{-1}$ and $(L-a)ML_n^{-1}$ depends on the oxidation states of the metal. When the metal exhibits only one oxidation state, the subsequent decomposition involves the elimination of even electron species so that even electron ions are produced (reactions II and V in the scheme). But when the metal
exhibits a lower oxidation state also, the subsequent decomposition processes can involve the elimination of even electron species and/or radicals (reactions I, III and IV)\textsuperscript{249,250}. Thus successive elimination of radicals does not occur when the metal exhibits only one oxidation state, as in the organic compounds, but successive elimination of radicals does occur when the metal exhibits a lower oxidation state also.

The elimination of even electron species from the molecular ion is more common in $\sigma$-bonded metal compounds than in organic compounds. A generalised fragmentation pattern is given in scheme II.

\begin{center}
\begin{tikzpicture}
    \node (A) at (0,0) {\(\text{ML}^+\text{n}\)};
    \node (B) at (-2,-2) {\(-\text{EENS} (2L)\)};
    \node (C) at (2,-2) {\(\text{VI}\)};
    \node (D) at (-2,-4) {\(\text{ML}^+\text{n-2}\)};
    \node (E) at (2,-4) {\(\text{VII}\)};
    \node (F) at (2,-6) {\(-\text{EENS (b)}\)};
    \node (G) at (2,-8) {\((\text{L-b})\text{ML}^+\text{n-1}\)};
    \draw [->] (A) -- (B);
    \draw [->] (A) -- (C);
    \draw [->] (A) -- (D);
    \draw [->] (A) -- (E);
    \draw [->] (A) -- (F);
    \draw [->] (A) -- (G);
\end{tikzpicture}
\end{center}

In most cases such eliminations involve rearrangement processes\textsuperscript{248 250} Elimination of type VI
involves cleavage of two metal ligand bonds. They are observed in the mass spectra of compounds derived from metals such as tin, gold, gallium etc., which exhibit two oxidation states separated by two units $^{251,253}$. The above facts have been interpreted in terms of the ability of the metal to change oxidation state. During the dissociation reaction electron transfer may be possible between the metal atom and the ligand in an ion, so that odd and even electron character of the ion is interchangeable (Valency change rule) $^{249,252}$. For example consider the ion $ML_n^+$, where the oxidation state of the metal is $n$. This ion is equivalent to $ML_n^{+}$, where the oxidation state of the metal is $(n-1)$, since an electron has passed from the ligand to metal. Several examples are available to illustrate the valency change concept $^{254-256}$. It is also noticed that in the mass spectra of metal compounds, where metal can exhibit more than one oxidation state, fragment corresponding to bare metal ion is formed.

Two examples for valency change concept are given below $^{268}$

1. $[\text{Sn}^{IV}(\text{CH}_3)_4]^+ \rightarrow [\text{Sn}^{IV}(\text{CH}_3)_3]^+ \rightarrow [\text{Sn}^{II}(\text{CH}_3)_2]^+$

2. $[\text{Sn}^{IV}(\text{C}_6\text{H}_5)_4]^+ \rightarrow [\text{Sn}^{II}(\text{C}_6\text{H}_5)_2]^+$ + $\text{C}_{12}\text{H}_{10}$
In the first case, successive elimination of radicals occurs. In the second, a concerted elimination of two ligand radicals takes place.

**FRAGMENTATION PATTERNS OF $\pi$-BONDED COMPOUNDS**

The fragmentation of $\pi$-bonded compounds chiefly involves metal ligand cleavage. But when the ligand is large or if it contains fragmentable substituents, cleavage in the ligand can also occur.

It is widely accepted that even and odd electron concept cannot be applied to complexes of this type. In mass spectroscopic terms, the molecular ions of $\pi$-bonded metal compounds can be classified as even electron species. That is, for electron counting the non-bonding electrons of the metal are excluded. Therefore these ions are excepted to fragment by losing even electron species so that an even electron ion is formed. In subsequent fragmentation also preferential loss of even electron species occurs. This behaviour has been observed generally, except in complexes.
containing only ligands such as NO and C₅H₅, which are odd electron species of great stability. For example, the molecular ion of C₅H₅MnC₆H₆ shows preferential loss of C₆H₆ rather than the loss of C₅H₅, which is an odd electron species²⁵⁷. Examples for the loss of even electron species from metal-bonded ligands, where π-bonding is present, are also available. It is also noticed that the fragmentation of metal-bonded ligands is often different from that of free ligand²⁵⁸,²⁵⁹.

RELATIVE BOND STABILITIES AND REARRANGEMENT PROCESSES

The mode of fragmentation of an ion depends on the relative stabilities of the bonds present in it. It can be assumed that the bonds which break readily are the weakest and most reactive in the chemical sense. In the σ-bonded compounds, the relative stabilities of its bonds determine the nature of the fragments. For example in the decomposition of molecular ions of trifluoroacetylacetone complexes the ions due to loss of CF₃ radicals are more abundant than the ions due to the loss of CH₃ radicals. This is in agreement with the accepted greater strength of the C-CH₃ bond, in comparison to C-CF₃ bond²⁶⁰. In (CH₃)₂SiCl₂ the ion CH₃SiCl₂ is more abundant than (CH₃)₂SiCl⁺. This observation is in agreement with the fact that dissociation
energies of Si-Cl is greater than that of Si-CH₃ bond\textsuperscript{261}.

It is established that in complexes having different ligands, some ligands are eliminated in preference to others. For example in nitrosyl carbonyl complexes the CO groups are eliminated first. In \(\Pi\)-hydrocarbon-metal nitrosyls the NO groups are lost first. In \(C_5H_5\)Mo(CO)\textsubscript{2} NO, both the CO groups are eliminated first. This is followed by the loss of NO. The elimination of \(C_5H_5\) does not occur\textsuperscript{262}. The donor-acceptor properties of the ligands determine type of behaviour. In \(\Pi\)-bonded complexes, metal to ligand back bonding is possible. If the positive charge is localised in the metal, in the ions derived from such compounds, the back bonding will be weakened. Therefore ligands which are weak donors, such as CO and NO are readily lost. But ligands whose donor properties are enhanced by the positive charge on the metal are held firmly.

Rearrangements are very common in the mass spectra of metal compounds. Most of the rearrangements occur via cyclic transition states. In general these rearrangements can be classified into two types.

i) \[
\begin{array}{c}
M \\
\downarrow \\
b \\
\downarrow \\
c \\
\end{array}
\]
\Rightarrow [M - C]^+ + a=b

ii) \[
\begin{array}{c}
M \\
\downarrow \\
d \\
\downarrow \\
c \\
\end{array}
\]
\Rightarrow [M - a - d]^+ + b=c
In the spectra of keto organo tins and methyl 4-trimethyl silyl butyrate, elimination of ethylene from molecular ions occurs and the mechanism is similar to McLafferty rearrangement \(^{263,264,245}\).

In complexes containing substituted \(\pi\)-bonded ligands, transfer of the substituent or part of it to the metal occurs in large number of cases. Such processes depend on the electronegativity of the group transferred to the metal. For example, in the spectra of compounds \(\text{CrC}_3\cdot\text{X}\), \([\text{X} = \text{F}, \text{Cl}, \text{Br} \text{ or I}]\) the abundance of the ions \(\text{CrX}^-\) increases from iodine to fluorine \(^{265}\). The separation between the metal and the group transferred also influences the rearrangements \(^{266}\).

Most of the rearrangements involve four-, five-, six-, or seven- membered cyclic transition states. But there are a few instances where higher membered transition state has been reported. For example in \(\alpha,\omega\)-bis (trimethyl silyl) ethers it is suggested that rearrangements involving upto forty nine membered cyclic transition state are possible \(^{267}\).

Many rearrangements which do not involve the formation of a new bond to the metal have also been postulated \(^{248}\).
The qualitative features of the mass spectra of several types of coordination compounds are discussed in this section.

As mentioned earlier, the mass spectra of organic compounds are dominated by even electron ions. The presence of transition metal introduces new features to the mass spectra of organic compounds, because of the ability of the metal to change valency. So far detailed studies in the mass spectra of coordination compounds with ligands having oxygen or nitrogen as donor atoms have been carried out. From these studies the following generalisations were arrived at:

1. A stable molecular ion is observed only in metal complexes where metal-ligand π bond exists. In other words, in cases where an increase in oxidation state for the metal can occur, the molecular ion will be stable. The molecular ion fragments by losing an even-electron species.

2. If the metal ion cannot undergo any change in oxidation state, the molecular ion will be relatively less abundant. In these cases, the fragmentation occurs by the elimination of a neutral radical followed by even electron neutral species.

3. If the metal ion can undergo a decrease in oxidation
state, the molecular ion will be absent or of weak intensity. Fragmentation proceeds by elimination of neutral radicals successively.

Mass spectra of metal complexes derived from $\beta$-diketones

Most of the mass spectral studies carried out on metal complexes have $\beta$-diketones or substituted $\beta$-diketones as ligands. Acetylacetonato complexes have received wide attention because of their volatile nature. The mass spectrum of Cr(acac)$_3$ was reported in 1957$^{269}$. But the first attempt to interpret the mass spectra of metal complexes was made only ten years later$^{248}$. It was found that for most compounds, the intense peaks were derived from monomeric forms of the complex. Ions derived from dimer and trimer were noticed in several cases, but with weaker intensity. The mass spectrum of calcium with acetylacetone as ligand deserves special mention since peaks of high intensity from dimer and trimer were recorded. The presence of ions corresponding to polymeric species in the mass spectra of acetylacetonato complexes of sodium, magnesium, calcium and strontium have also been reported in another study$^{270}$. Negative ion mass spectra were obtained for the calcium, cobalt and copper complexes$^{248}$. The possible fragmentation
schemes have been discussed for complexes of the types \( \text{M(acac)}_2 \), \( \text{M(acac)}_3 \) and \( \text{M(acac)}_4 \).

Some of the recent mass spectral studies of \( \beta \)-diketonato complexes of various metals include electron impact mass spectra of bis (acetyl acetonato) dioxouranium, characterisation of certain vanadium (IV) \( \beta \)-diketonate complexes by mass spectra, acute pressure dependence of the electron ionisation mass spectrum of molybdenyl acetyl acetonate, mass spectra of uranyl \( \beta \)-diketones and their adducts with trimethyl phosphine oxide, and that of neptunium (IV) and neptunium (VI) \( \beta \)-diketonates. In another study it was found that \( \text{Fe(acac)}_3 \) and \( \text{Al(acac)}_3 \) give a series of doubly charged ions in their electron impact mass spectra. The formation of doubly charged ions is discussed on the basis of odd-even electron rule and the tendency of ion to change the valency. Cluster ions were encountered in the electron and chemical ionisation mass spectra of transition metal acetyl acetonates. The mass spectra of these complexes were recorded under conditions that maximise the abundance of cluster ions. It was found that these ions contain two or more metal atoms. Fragmentation patterns of some acetylacetonate (carbonyl) rhodium compounds have been reported in another study.

The mass spectra of several metal complexes derived from dibenzoyl methane (1,3-diphenyl propane-1,3-
dione) were studied in detail. Possible fragmentation pathways for complexes of the type $M(dbm)_3$ [$M = Al, Si, Cr, Fe, Y$] and $M(dbm)_2$ [$M = Be, Mg, VO, Co, Ni, Cu, Zn$] were proposed by several workers. The results illustrate the influence of metal ions on the mass spectrum by its ability to undergo changes in oxidation state.

Interesting results on the spectra of metal complexes derived from fluorine-substituted $\beta$-diketones have been reported. These complexes are stable and volatile for gas chromatographic analysis. Therefore, they are important from an analytical point of view. The mass spectrometric behaviour of these complexes are useful so that GLC eluants can be identified. The spectra were found to be different from those of simple $\beta$-diketone complexes due to the presence of fluorine atoms. Interesting ion dissociation reactions were observed in the mass spectra of metal complexes prepared from fluorine substituted acetylacetonates. Similar reactions were absent in the case of simple acetyl acetonato complexes. Prominent metastable peaks support this observation. The mass spectra of some of the complexes provide evidence for the formation of metal fluorine bonds in the fluorine transfer reactions and also proof for valency change concept. For example in the mass spectra of $M(hf acac)_3$ [$M = Al, Cr, Fe, Co$; $hfacac = hexa fluoro acetylacetone$], metastable
peaks due to the formation of AlF₃, CrF₃, FeF₃, FeF₂ and CoF₂ from the appropriate metal containing fragment ion were observed. Formation of FeF₂ and CoF₂ indicates the reduction of metal.

The following conclusions were arrived from the mass spectral studies of metal complexes derived from tri- and hexa fluoroacetylacetones.

1. When the metal exhibits a formal increase in oxidation state, the molecular ion is of high intensity
2. For metal complexes derived from tri-fluoro acetylacetone, ions produced by elimination of CF₃ radicals are more abundant than those produced by elimination of CH₃ radicals.
3. In the complexes derived from acetylacetone, ions formed from a decrease of the oxidation state of the metal are more prominent.
4. The extent of fragmentation is more in fluorine substituted acetylacetonato complexes when compared to simple acetylacetonato complexes.

This must be due to the decrease in the metal-oxygen bond strength of the former. The stability constants of fluorine substituted acetylacetonato complexes are less and, therefore metal-oxygen bond strength will decrease.
The mass spectra of complexes derived from 1-trifluoro methyl 3-aryl-1,3-diones and from N-phenyl-2-carbonyl-dimedone have been reported\textsuperscript{252,283}. The fragmentation patterns were found to be similar to those of the complexes discussed above.

In another study, the mass spectra of trichloroacetylacetonates of divalent cations Be\textsuperscript{2+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+} and UO\textsuperscript{2+} were recorded\textsuperscript{284}. The results were compared with those of homologous fluorinated complexes. Transfer of chlorine to the metal was observed during fragmentation just like fluorine transfer to the metal in fluorinated acetylacetonato complexes. The mass spectra of lanthanide chelates of fluorinated \(\beta\)-diketones are interesting\textsuperscript{285}. Valency change from +3 to +2 occurred with samarium, thulium, europium and ytterbium. From the intensity of metal containing peaks the tendency to get reduced was studied. In the case of cerium, the valency was found to change from +4 to +3.

Reports on the mass spectra of metal complexes of trifluoro alkyl-\(\beta\)-diketones deals with the atom and group migration from the ligand to the metal. It is found that fluorine or alkyl group migration to the metal depends on whether the metal belongs to class a or class b. Class a metals with no d electrons showed fluorine migration while class a metals with a \(d^{10}\) configuration showed both
flourine and alkyl group migration. The chelates of class b metals showed only the alkyl group migration to the metal\textsuperscript{286,287}.

Mass spectra of a variety of fluorinated tetrakis ($\beta$-diketone) complexes of zirconium are reported recently\textsuperscript{288}. The fragmentation pattern showed stepwise loss of entire $\beta$-diketonate ligands. As in the case of a number of fluorinated $\beta$-diketonate complexes of other metals, here also the mass spectra demonstrated fluorine transfer to zirconium from the ligand.

In addition to these, literature on the mass spectra of complexes of substituted $\beta$-diketones, in which the fragmentation behaviour is different is also available. For example, in the chromium complex of 3-nitropentene-2,4-dione, the most prominent ions correspond to the oxo or hydroxo species\textsuperscript{289}. The mass spectrum of does not give a molecular ion. This is due to the easy cleavage of Ti-I bond\textsuperscript{290}. The complexes Cu(acac) DPPH and Cu(tfacac) DPPH [DPPH = 2,2-diphenyl-1-picrylhydrazil] do not exhibit molecular ions\textsuperscript{291}. Prominent ions resulted by the fragmentation of DPPH. The mass spectra of a number of compounds of the type (C\textsubscript{8}H\textsubscript{12}-diketonyl) M ($\beta$-diketonate), where M = Pd or Pt have been reported\textsuperscript{292}. In these complexes, major peaks correspond to the loss of a $\beta$-diketone molecule. In the mass spectra of PtX(acaac)(C\textsubscript{2}H\textsubscript{4}), where X =
Cl or Br, strong peaks corresponding to the loss of ethylene molecule or halogen were observed\textsuperscript{293}.

Recently the mass spectrum of bis (acetylacetonato) dioxouranium (VI) was studied and the results were compared with those of manganese, iron, cobalt, nickel and copper complexes\textsuperscript{271}.

Chemical ionisation mass spectra of acetylacetonato complexes are also reported. These spectra are obtained using isobutane as the reagent gas\textsuperscript{294}. Complexes of divalent iron, cobalt and nickel gave the [P + 1] ion as the most abundant ion. Another interesting feature of chemical ionisation spectra was the presence of ions with general formula

\[ [M_n\cdot\text{acac}_{2n-1}]^+ \text{ or } [M_n\cdot\text{acac}_{3n-1}]^+ \]

Mechanisms are also proposed for the formation of such polymeric ions.

\section*{Mass Spectra of Metal Complexes Derived from Schiff Bases and Related Compounds}

Characterisation of a number of metal complexes of schiff bases have been carried out with the help of mass spectra. Earlier studies include the mass spectra of N - substituted salicylaldimine complexes of iron, nickel and manganese. In the spectra of FeL\_3, FeL\_2, FeL\_2Cl and
(FeL₂)₂O, where L = Sal-N-nPr, the molecular ions were found to be weak. The most abundant ion was found to be Fe(Sal-N-nPr)²⁺. The manganese complexes MnL₃, MnL₂Br and MnL₂ (acetate) also gave molecular ions of weak intensity. It is interesting to note that each of these complexes gave peaks corresponding to ions with two manganese atoms. Strong molecular ion peaks were observed in the case of Ni(Sal-N-R)₂ complexes. [R=C₂H₅, i-C₃H₇, i-C₄H₉ and C₆H₅]. An unusual feature of the spectra of these complexes is the presence of peaks corresponding to the species (L Ni H)⁺. Similar peaks were noted in the spectra of acetyacetonato complexes of Ni(II). But the mechanism of hydrogen transfer is studied only in the latter. The mass spectra of metal complexes prepared from schiff bases formed by condensation of (a) an aliphatic diamine with an aromatic aldehyde, (b) a diamine with pyrrole-2-carbaldehyde and (c) one mole of ethylene diamine with two moles of benzoyl acetone have been studied in detail.

In all these complexes, the molecular ion peaks were observed and were found to be the base peak. The fragmentation patterns of these complexes were found to be similar. Complexes prepared from β-diketone-ethylene diamines have been used for the analytical determination of metals by gas chromatography and mass spectrometry. The mass spectra of several nickel (II) complexes of macrocyclic...
schiff bases have also been reported. In these spectra, the molecular ions were found to be scarce and the corresponding peaks, therefore, were weak.

**MASS SPECTRA OF METAL COMPLEXES OF OXINATES AND RELATED LIGANDS**

The mass spectra of 8-hydroxy quinoline complexes were studied in detail. The spectra of aluminium, scandium, gallium, indium, chromium and iron complexes were recorded. It is found that the molecular ion fragments by losing a ligand radical to give $M(OX)_2^+$. This ion forms the base peak in all the complexes. It was noticed that when the metal ions have stable oxidation states lower than +3, further fragmentation gives a large number of ions. For example, gallium and indium can exhibit +1 oxidation state in addition to +3 state. Metal containing ions with the metal in +1 oxidation state were found to be abundant in the case of gallium and indium complexes.

The mass spectra of mixed ligand complexes of titanium, zirconium and hafnium with halogen, cyclopentadienyl and oxine as ligands were also reported. In these the molecular ion peaks were either absent or very weak. It was also noticed that zirconium and hafnium complexes exhibit much less fragments than titanium complex.
Mass spectra of nickel (II) and copper (II) complexes derived from 4-substituted benzoquinone mono oximes and nickel (II) and palladium (II) complexes derived from vic-dioximes have also been reported\textsuperscript{309-311}. Ions derived from polymeric species were present in some cases. The mass spectra of vic-dioxime complexes were found to be similar to those of nickel (II), palladium (II) and platinum (II) complexes derived from dimethyl glyoxime, diphenyl glyoxime, 1,2-cyclohexanedione dioxime and -furyldioxime obtained in a separate study.

It is interesting to note that nickel could be detected at the picogram level as the dimethyl glyoximate by integrated ion current technique\textsuperscript{312}.

Negative and positive ion chemical ionisation mass spectra of several dioximes and their nickel (II) complexes have also been reported\textsuperscript{322}.

MASS SPECTRA OF COMPLEXES DERIVED FROM LIGANDS CONTAINING SULPHUR AND PHOSPHORUS

Some of the early studies include the mass spectra of nickel (II) complexes derived from dialkyl dithiophosphates and their adducts with 2,2'-bipyridyl and 1,10-phenanthroline and the mass spectra of some -diketone-bis (thiosemicarbazone) complexes of copper (II)\textsuperscript{313-315}.
The thermal and photolytic addition of sulphur to nickel and zinc dithiobenzoates was studied by mass spectrometry, using sulphur-34 as a label\textsuperscript{316}.

Mass spectral data for tris- and bis (N,N-dialkylidithiocarbamato) complexes of chromium, iron, cobalt, ruthenium, rhodium and thallium were reported by K.W. Given \textit{et al.}. Fragmentation mechanisms were discussed in detail by them\textsuperscript{317}.

Dithiophosphato complexes have received wide attention for mass spectral studies. Complexes of the type $[(R_2PS)_2]_2Ni$, were P = C\textsubscript{6}H\textsubscript{5}, o-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4}, m-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4}, p-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4}, m-ClC\textsubscript{6}H\textsubscript{4} and p-ClC\textsubscript{6}H\textsubscript{4} have been subjected to mass spectral studies\textsuperscript{316}. In another study the fragmentation reactions of planar, tetrahedral, octahedral and oligomeric metal dithio phosphinates were established by mass spectrometry\textsuperscript{319}. The complexes studied were $M(II)L_2$, $[L=(C_2H_5)_2PS_2$, $M = Zn, Cd, Hg, Pb, Co, Mn, Ni, Pd and Pt]$, $M(III)L_3$, $[M = Sb, Bi, In, Rh and Ir]$ and $[M(I)L]_n$. In the last, $M = Tl$; $n = 1$, $M = Au$; $n = 2$ and $M = Cu$; $n = 4$. The dependence of fragmentation on the ionisation energy of the metal and metal-ligand $\pi$-bonding were discussed. It is also found that oligomeric complexes show strong metal-metal interaction even under electron impact.

Mass spectrometric studies of diaryl dithiophosphato complexes of thallium (I) and dialkyl dithio-
phosphato complexes of tin (II) and lead (II) have also been carried out$^{320,321}$. Loss of ligand radicals followed by the elimination of neutral species such as R-H, H$_2$O, H$_2$S etc. from the molecular ions of tin (II) and lead (II) complexes were observed.

Characterisation of several dithiolato, diselenolato and diseleno carbamato complexes of cobalt (III) was done mass spectrometrically$^{323,328}$. Investigations of mixed ligand cobalt dithiocarbamate complexes and studies on exchange and redox reactions of mercury dithiocarbamate complexes were carried out with the help of mass spectrometry$^{324,325}$. Mass spectral studies of some iron (III) binuclear complexes with bridging thiuram disulphide ligands, and six diverse chelate derivatives of nickel (II), copper (II), copper (III) and chromium (III) ions with sulphur as donor atom, are also available$^{326,327}$. Diethylphosphino gallium (III) and indium (III) complexes were studied by mass spectrometry and the spectra revealed a trimeric form for the complexes$^{329}$. The mass spectra of several square planar complexes of platinum were studied with the aim of determining whether there were significant differences between the spectra of cis and trans isomers$^{330}$. The mass spectra of dihalodiphosphine complexes showed marked
differences between cis and trans isomers. Thus the differences indicated the retention of the square planar geometry in the molecular ion. The mass spectra of a number of square planar dichlorodiphosphine platinum complexes having mixed substituents in the phosphine ligand have been reported. Negative ion mass spectrum was obtained for the complex $[\text{PtCl}_2\text{P(C}_2\text{H}_5)_3\text{]}_2^-$ \textsuperscript{332}. The spectrum revealed the production of a five coordinated complex, $[\text{PtCl}_3\text{P(C}_2\text{H}_5)_3\text{]}^-$ \textsuperscript{332}. An analogous five coordinate complex $[\text{PtCl}_2\text{I(P(C}_2\text{H}_5)_3\text{)}_2]^-$ was produced in the presence of CH$_3$I.

Mass spectra of carboxylates and related complexes

Several carboxylate complexes of copper (I) were found by mass spectrometry to be dimeric in vapour state. The molecular ions were found to be stable. It was found that presence of electron withdrawing groups destabilise the molecular ion, their relative intensities being lowest when fluorine containing substituents were present. Migrations of fluorine and hydrogen also occurred. The mass spectra of basic zinc carboxylates and those of related beryllium carboxylates were also reported.

Copper (II) methoxocarboxylato complexes and carboxylates of platinum group metals were studied by mass spectrometry and useful informations about their structures
Mass spectra of miscellaneous metal complexes

EDTA complexes of alkali, alkaline earth, and transition metals were studied by FAB mass spectrometry. Attempts were made to correlate the peak intensities with atomic size of the metals. In another study the structure analysis of EDTA complex of nickel (II) was carried out by FAE mass spectrometry\(^{340,341}\).

Study of preferential platination of equimolecular DNA-RNA mixture in solution was carried out by electron impact pyrolytic mass spectrometry\(^{342}\). The results showed that the complexation of an equimolecular DNA-RNA mixture by cisplatin led to 20% preferential binding to DNA. Three classes of Pt-DNA complexes were also studied by a combination of pyrolysis and electron impact mass spectroscopy\(^{343}\).

Doubly charged ions were observed in some ruthenium (II) complexes of general formulae \([\text{Ru}L'\text{L}']X_2\), \([\text{RuL}_2\text{L}']X_2\) and \([\text{RuL}_3]X_3\). \(L, L', L''\) include 2,2'-bipyridine, 1,10-phenanthroline and their derivatives. Ions of the type \([\text{RuL}_3]^{2+}\), \([\text{RuLL}'\text{L}'']^{2+}\) and \([\text{RuL}_2\text{L}']^{3+}\) were observed in the mass spectra\(^{344}\). Fast atom bombardment method was used to record the mass spectra. Copper (II), silver (I) and thallium (I)
complexes of 1,10-phenanthroline, 2,2'-bipyridine and their derivatives were also characterised by FAB mass spectroscopy\textsuperscript{345}.

Some other reports of interest include the thermal decomposition and mass spectral studies of trans [pseudo halo (imidazole) bis (dimethylglyoximato)] cobalt (III), mass spectra of simple tetraza macrocyclic complexes and their acyclic derivatives, secondary ion mass spectrometry of non-volatile isocyanide complexes of silver (I) and copper (I), FAB mass spectrometry of neutral and ionic platinum (II) pyrazole derivatives and the mass spectrometric behaviour of some iridium (I) and iridium (III) pyrazolate derivatives\textsuperscript{346-350}. 