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Metal Valency Effects in the Mass Spectra of Co-ordination Compounds

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THE value of mass spectrometry in studies with organic compounds is now well known. The technique is of increasing importance for metal co-ordination compounds, *e.g.* phthalocyanins,[1] porphyrins,[2,3] π-cyclopentadienyl complexes,[4–7] metal carbonyls,[8,9] metal halides,[10,11] and Schiff base complexes, dithiocarbamates, acetylacetonates, etc.[12] The mass spectra of some of these compounds can be best rationalized if changes of valency of the bonded metal atom are assumed to occur during the ion dissociation reactions. In fact, the mode of dissociation of a metal complex ion may be markedly dependent on the valency states normally assumed by the metal concerned. For example, if a radical ion $[X{-}M{-}Y]^{+\cdot}$ where M is a metal atom of valency state n, loses a radical $Y\cdot$ the resulting positive ion $[X{-}M]^{+}$ is equivalent to the radical ion $[X{-}M]^{+\cdot}$ where M is now in the valency state $(n - 1)$, an electron being supposed to pass from the group X into the metal atom.[13] This lower-valent radical ion could then undergo further radical-ion reactions. Alternatively, the initial radical ion $[X{-}M{-}Y]^{+\cdot}$ might lose a neutral molecule, *e.g.* XY, giving $[M]^{+\cdot}$ in which M now has valency state $(n - 2)$. This phenomenon can be illustrated by the following four examples.

(1) Ferric chloride and auric chloride vapours have similar dimeric structures[14] but distinctly different mass spectra. The spectrum of Au_2Cl_6 shows abundant ions and metastable ions due to consecutive elimination from the molecular ion of two chlorine *molecules*, whereas the spectrum of Fe_2Cl_6 shows ions due to the consecutive loss from the molecular ion of two chlorine *atoms*. The different behaviour may be related to the different possible valency changes, namely $Fe^{III} \rightarrow Fe^{II}$ and

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[1] H. C. Hill and R. I. Reed, *Tetrahedron*, 1964, **20**, 1359.

[2] H. Budzikiewicz, C. Djerassi, A. H. Jackson, G. W. Kenner, D. J. Newman and J. M. Wilson, *J.*, 1964, 1949.

[3] J. E. Falk, J. N. Phillips and J. S. Shannon, unpublished work.

[4] L. Friedman, A. P. Irsa and G. Wilkinson, *J. Amer. Chem. Soc.*, 1955, **77**, 3689.

[5] A. F. Reid, J. S. Shannon, J. M. Swan and P. C. Wailes, *Austral. J. Chem.*, 1965, **18**, in the press.

[6] R. I. Reed and F. M. Fabrizi, *Applied Spectroscopy*, 1963, **17**, 124.

[7] A. Mandelbaum and M. Cais, *Tetrahedron Letters*. 1964, No. 51, 3847.

[8] H. H. Hoehn, L. Pratt, K. F. Watterson and G. Wilkinson, *J.*, 1961, 2738.

[9] H. S. Ang, J. S. Shannon and B. O. West, *Proc. Chem. Soc.*, in the press.

[10] R. I. Reed, "Ion Production by Electron Impact", Academic Press, London, 1962, and refs. cited therein.

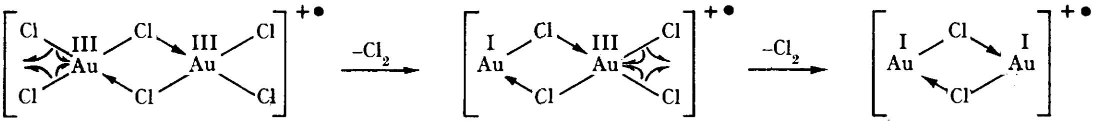
[11] J. S. Shannon, unpublished work.

[12] J. S. Shannon, Paper to Australian Metal-Organic Symposium, Royal Australian Chemical Institute, Melbourne, May 1964.

[13] The symbolism $(\quad)^{+\cdot}$ is used for odd-electron ions (see J. S. Shannon, *Proc. Roy. Austral. Chem. Inst.*, 1964, **31**, 323). It is assumed here that the metal atom M contains an even number of electrons in the parent compound.

[14] J. C. Bailar, "The Chemistry of the Co-ordination Compounds", Reinhold, New York, 1956, p. 365.

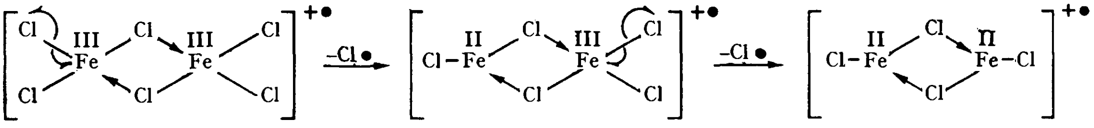
$\mathrm{Au^{III}} \rightarrow \mathrm{Au^{I}}$, during the ion reactions. For example:



m/e 604 (28%)* (Cl=35)

m/e 534 (57%)

m/e 464 (100%)



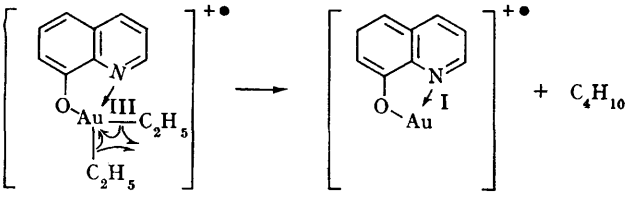
m/e 322 (12%)

m/e 287 (48%)

m/e 252 (100%)

* Abundance relative to base peak.

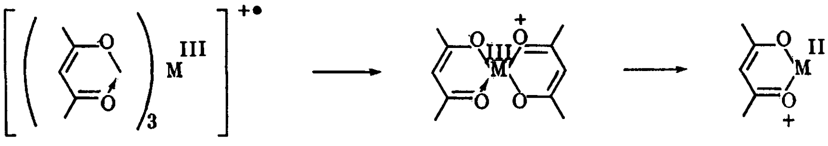
(2) The influence of the change $\mathrm{Au^{III}} \rightarrow \mathrm{Au^{I}}$ is further demonstrated by the spectrum of diethylauric oxinate, which has its base peak at m/e 341 and a metastable peak at m/e 291·4 due to the transition $399^{+\bullet} \rightarrow 341^{+\bullet} + 58$. Thus, as with Au_2Cl_6, we have the unusual phenomenon of the concerted elimination of two radicals which are initially attached to the same atom, *viz.*:



m/e 399 (8°)

m/e 341 (100%)

(3) Both ferric and aluminium acetylacetonates give molecular ions and very abundant ions due to the loss of one ligand radical. However, only the ferric compound gives an ion due to the loss of two ligand radicals, owing presumably to the readiness of the iron atom but not the aluminium atom to take on a bivalent form:



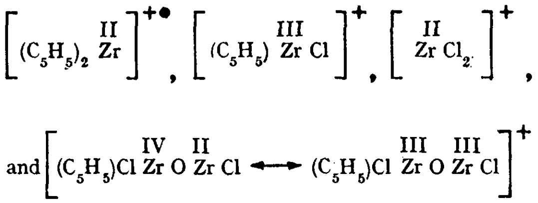
m/e 353 (19%) M=Fe
m/e 324 (10%) M=Al

m/e 254 (100%) M=Fe
m/e 225 (100%) M=Al

m/e 155 (40%) M=Fe
m/e 126 (0%) M=Al

(4) Di-, tri-, and tetra-valent zirconium compounds are known, and in the mass spectra of dichloridodi(cyclopentadienyl)zirconium dichloride and of the related bridged oxide, bis[chloridodi(cyclopentadienyl)zirconium] oxide,[5] a number of ions are observed in which the only plausible structures require the zirconium atom or atoms

to have undergone reduction to the +3 and +2 valency states. For example:



$$\left[(C_5H_5)_2\overset{II}{Zr}\right]^{+\bullet},\quad\left[(C_5H_5)\overset{III}{Zr}Cl\right]^{+},\quad\left[\overset{II}{Zr}Cl_2\right]^{+},$$

$$\text{and}\left[(C_5H_5)Cl\overset{IV}{Zr}O\overset{II}{Zr}Cl \longleftrightarrow (C_5H_5)Cl\overset{III}{Zr}O\overset{III}{Zr}Cl\right]^{+}$$

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