

## Mass Spectra of Fluorinated Acetylacetonate Complexes

By C. REICHERT, J. B. WESTMORE,\* and H. D. GESSER

(Department of Chemistry, University of Manitoba, Winnipeg, Canada)

FLUORINATED ACETYLACETONATE complexes of metals are currently of great interest because of their volatility and consequent use in analysis of metals by gas chromatography.<sup>1</sup> With the development of commercial instruments involving the tandem operation of a gas chromatograph and a mass spectrometer it seems desirable to attempt to determine the factors which influence the fragmentation of the metal chelate under electron impact.

Some of the more significant major peaks in the spectra of a number of compounds are given in the Table, where hfa = hexafluoroacetylacetonate, tfa = trifluoroacetylacetonate, and *P* = parent, or molecular, ion. In assigning the base peak, mass 69 (CF<sub>3</sub><sup>+</sup>), which was often the most abundant peak, was ignored. The metals selected for discussion include one which readily undergoes valency changes, and two which do not, one bi- and the other ter-valent.

The results are consistent with the ready loss of one odd-electron neutral fragment, after which further odd-electron neutral fragments are not readily lost unless the metal can undergo a valency change (as in the case of Cu in which the ion *P*-138 is well developed). When no further odd-electron neutral fragments can be easily lost, then loss of even-electron fragments can occur, as shown in the Scheme. Most of the processes could be confirmed by the presence of peaks due to metastable ions and

TABLE

Major peaks, as percentage of base peak, in the mass spectrum of the metal chelates

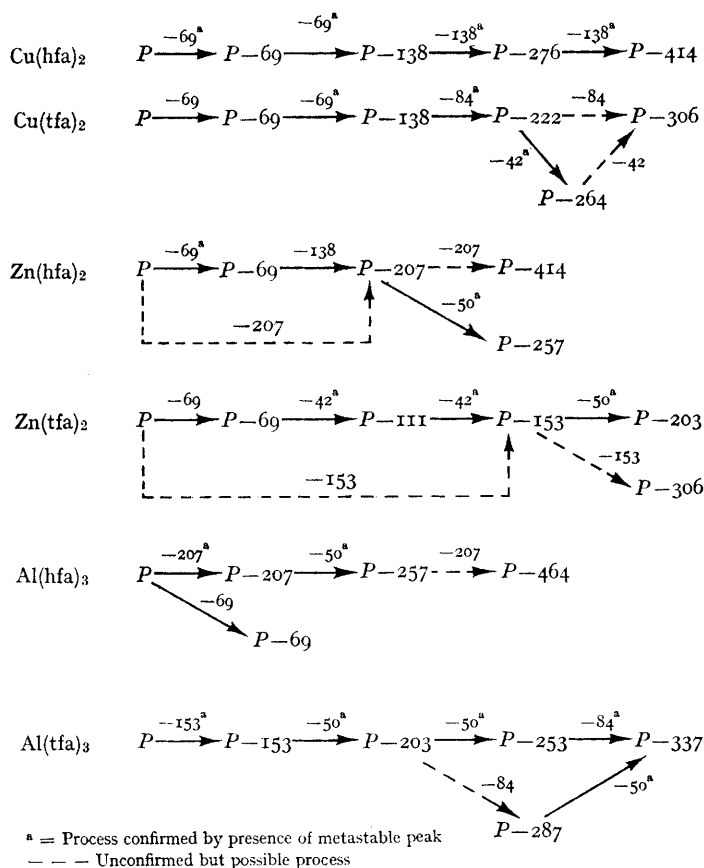
	Cu(hfa) <sub>2</sub>	Zn(hfa) <sub>2</sub>	Al(hfa) <sub>3</sub>
<i>P</i>	9.5	8.9	5.4
<i>P</i> -69	23.7	26.6	6.0
<i>P</i> -138	22.8	2.5	—
<i>P</i> -207	1.5	18.6	100.0
<i>P</i> -257	—	100.0	17.1
<i>P</i> -276	100.0	11.7	2.8
<i>P</i> -373	11.0	6.0	—
<i>P</i> -414	82.0	46.1	—
<i>P</i> -464	—	—	11.2
<i>P</i> -479	—	—	7.1
	Cu(tfa) <sub>2</sub>	Zn(tfa) <sub>2</sub>	Al(tfa) <sub>3</sub>
<i>P</i>	5.1	44.0	3.4
<i>P</i> -15	1.2	21.0	—
<i>P</i> -69	10.6	100.0	—
<i>P</i> -111	—	40.3	—
<i>P</i> -138	27.3	—	—
<i>P</i> -153	8.2	54.2	100.0
<i>P</i> -168	10.0	—	—
<i>P</i> -181	—	9.1	—
<i>P</i> -203	—	66.7	9.4
<i>P</i> -222	100.0	9.1	1.5
<i>P</i> -253	—	—	7.2
<i>P</i> -264	59.1	—	—
<i>P</i> -265	18.4	11.6	—
<i>P</i> -287	—	—	12.2
<i>P</i> -306	44.4	28.2	2.7
<i>P</i> -337	—	—	38.8

by measuring heights of isotopic peaks. In the case of Cu(hfa)<sub>2</sub> additional confirmation was

obtained by addition of  $D_2O$  to the reservoir containing the gaseous sample when slow deuterium exchange occurred.

The process is accompanied by the appearance of a strong metastable peak in all cases observed.

Samples were prepared by standard methods and



In bis-chelates, the odd-electron neutral fragment lost is  $\bullet CF_3$  (69) in preference to  $\bullet CH_3$ , while in tris-chelates the whole ligand radical is lost (hfa, 207; tfa, 153). Corresponding processes occur in the acetylacetonates.<sup>2</sup> The even-electron neutral fragments lost are  $CF_3 \cdot CO \cdot CH \cdot CO$  (138),  $CF_2$  (50),  $CH_3 \cdot CO \cdot CH \cdot CO$  (84), and  $CH_2 \cdot CO$  (42). Loss of the last two occurs in the acetylacetonates, but loss of  $CF_2$  appears to be novel, and presumably occurs with migration of a fluorine atom to the metal.

purified by several sublimations. Mass spectra were recorded on a Hitachi RMU-6D single-focussing mass spectrometer using electrons of 50v energy. Samples were introduced either through a heated inlet system or by direct insertion into the ion source through a vacuum lock. The method of sample introduction seemed to cause little difference in the recorded spectra.

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<sup>1</sup> For a Review see R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates", Pergamon Press, Oxford, 1965.

<sup>2</sup> C. G. MacDonald and J. S. Shannon, *Austral. J. Chem.*, 1966, **19**, 1545; J. Macklin and G. Dudek, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 403; S. Sasaki, Y. Itagaki, T. Kwokawa, K. Nakanishi, and A. Kasahara, *Bull. Chem. Soc. Japan*, 1967, **40**, 76.