

MASS SPECTROMETRIC STUDY OF B-DIKETONE COMPLEXES

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The mass spectra of hexafluoroacetylacetonates show that odd-electron ions tend to fragment by the elimination of odd-electron neutral radicals with the formation of even-electron fragment ions. Even-electron ions tend to fragment to loss even-electron neutral fragment. Metals that can change valency by one unit and consequently reverse their odd-or even-electron character tend to fragment differently than metals that do not change valency. Loss of neutral metal fluorides is observed in Ni and Mn complexes, and are supported with metastable peaks. Peaks above the parent peak in Mn (hfac)₂ are noted:

INTRODUCTION

The literature in the field of mass spectrometric indicates that fragmentation patterns of the compounds of metal B-diketonates are available only for the common metal acetyl-acetonates MacDonald and Shannon (1966) and for a few trifluoro and hexafluoroacetyl-acetonates Holtclaw *et al.* (1969). This limited investigation has already led to some generalization about these complexes. It appears that for a given ligand, the nature of the fragmentation pattern is influenced by the ability of the chelate metal to change oxidation state. The following study further confirmed this idea.

MATERIALS AND METHODS

The ligands here reported have the general formula $\text{CF}_3-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{R}$. These were prepared by the method of Reid and Calvin (1930). The metal complexes were purified by crystallization (95 per cent ethyl alcohol) or by sublimation. Samples purified by crystallization were subsequently sublimed.

Fragmentation patterns including metastable peaks were determined

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for Cu, Ni, Mn and Zn hexafluoroacetyl-acetonates at an accelerating voltage of 900 V, an electron potential of 70 eV, and an oven temperature 60°C.

RESULTS AND DISCUSSION

The fragmentation patterns of Cu, Ni, Mn and Zn hexafluoroacetylacetonates are given in Table 1 to 4. Schemes 1-4 show decomposition pathways.

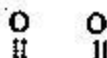
The first step in the electron impact of these compounds is the loss of an electron to give the parent ion (molecular) as shown in Schemes 1-4. Subsequent fragmentation as discussed and generalized by McDonald and Shannon, depend upon:

- (1) odd or even electron character of an ion,
- (2) the ability of the metal to change its valency state.

Our results are consistent with the above postulates. Loss of odd electron neutral fragment CF_3 is observed in each case from odd electron species $(^*)ML_2^+$, which gave an even electron species $(ML_2-CF_3)^+$. (Schemes 1-4). Further loss of odd electron species is not expected until the metal can undergo a valency change. Thus Cu^{+2} which easily reduces to Cu^{+1} gave further loss of CF_3 . The consecutive loss of two CF_3 is not observed in any other metal.

The loss of even electron fragment CF_2 from even electron species $(ML_2-F)^+$ is observed in Cu, Ni and Mn.

Loss of even electron species $(L-CF_3)$ is observed from $(ML_2-CF_3)^+$ as expected. Loss of CF_2 from this even electron species is observed only in case of Ni. However, loss of CF_2 from ML^+ is observed in Zn, Mn and Ni. Loss of $-(L-F)$ is observed from $(ML_2-CF_3)^+$ in Ni and Mn.



The elimination of CF_2 and $CF_3-C-CH-C-CF_2$ (Schemes 1-4) require a fluorine rearrangement. Plausible acceptor sites for the fluorine include the electron deficient carbon (generated as the $C-CF_3$ or CF_2-F bonds are broken) and the metal atom. Our study supported that fluorine migrates to the metal. Loss of neutral metal fluorides is observed in Mn and Ni. (Schemes 2,4). Each process is confirmed by metastable peaks.

The fluorine rearrangement reactions with the loss of neutral metal

fluorides suggest that the oxidation state of the metal has not been reduced. For example, the elimination of NiF_2 and MnF_2 give indication that these metals are not changed from +2 to +1.

Predominant peaks above the parent peak of $\text{Mn}(\text{hfac})_2$ ($m/e = 731$, 676, 657, 607, 538, 488 corresponding to $[(\text{MnL}_2)_2\text{-L}]^+$, MnL_3^+ , $(\text{MnL}_3\text{-F})^+$, $\text{MnL}_3\text{-CF}_3^+$, $[\text{MnL}_3\text{-(L-CF}_3)]^+$, $(\text{MnL}_3\text{F})^+$ are noted at 450, 600, 900, 1200, 1800, 2400 accelerating voltages. These peaks of sublimed complex have not been reported in the literature with any divalent fluorinated complexes. Whether the original material is in the polymerized form or these ions are formed in the mass spectrometer is a question for discussion.

It may be noted that the B-diketonates may serve as model compounds for biologically important and other complex metallo-organic chelates. Information gained from model metal chelates systems may well form the basis for spectro-metric structural analysis of naturally occurring metal chelates.

TABLE 1. *Relative Peak Heights** $\text{Cu}(\text{hfac})_2$

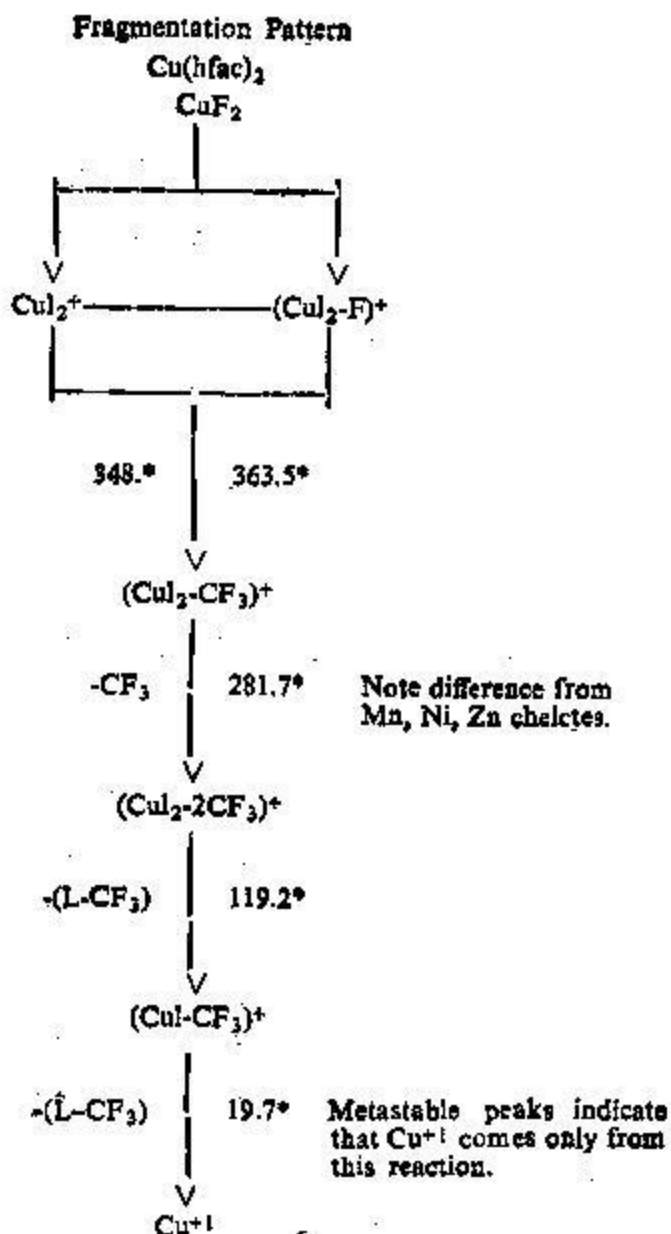
The following relative peak heights (R.P.H.) for major peaks in Cu hexafluoroacetylacetonate were observed.

Fragment	m/e	(a) R. P. H.		
CuL_2^+	477	22.1	22.01	21.90
$(\text{CuL}_2\text{-CF}_3)^+$	408	37.45	37.25	37.53
$(\text{CuL}_2\text{-2CF}_3)^+$	339	23.77	23.67	23.09
$(\text{CuL-CF}_3)^+$	201	100	100	100
$(\text{LH-CF}_3)^+$	139	70.25	70.29	70.19
$(\text{L-CF}_3\text{-F})^+$	119	19.33	18.45	18.86
Cu^{+1}	63	35.50	34.90	35.30
Doubly charged ions				
$\text{CuL}_2\text{-2CF}_3^{++}$	169.5			
CuL_2^{++}	238.5			

(a) For this one example three different determinations are presented to demonstrate the reproducibility of the data.

* $\text{L} = \text{hfac} = \text{hexafluoroacetylacetonate}$. α R.P.H. β Relative Peak Heights

SCHEME 1



Symbols: — Path confirmed by metastable peak.

— Path not confirmed by metastable peak.

L Ligand portion of the complex.

* m/e of metastable ion.

TABLE 2
 $\text{Ni}(\text{hfac})_2$

Fragment	m/e	R.P.H
NiL_2^+	472	54.1
$\text{NiL}_2\text{-CF}_3^+$	403	100
$\text{NiL}_2\text{-2CF}_3^+$	334	1.7
NiLF^+	284	85.3
NiL^+	265	61.0
NiL-CF_2^+	215	81.2
L-2HF^+	167	38.6
LH-CF_3^+	139	32.5
$\text{L-CF}_3\text{-F}^+$	119	18.9
$\text{L-CF}_3\text{-F-CO}^+$	91	15.6
CF_3^+	69	18.4
Doubly charged ions		
$\text{NiL}_2\text{-F}^{++}$	226.5	
$\text{NiL}_2\text{-CF}_3^{++}$	201.5	

TABLE 3
 $\text{Zn}(\text{hfac})_2$

Fragment	m/e	R.P.H
ZnL_2^+	478	23.8
$\text{ZnL}_2\text{-CF}_3^+$	409	100
$\text{ZnL}_2\text{-2CF}_3^+$	340	5.38
ZnL^+	271	15.59
ZnL-CF_3^+	202	11.7
LH^+	209	63-37
L-2F^+	169	58.67
LH-CF_3^+	139	29.9
$\text{L-CF}_3\text{-F}^+$	119	99.7
$\text{L-CF}_3\text{-F-CO}^+$	91	34.8
CF_3^+	69	17.4
Doubly charged ion		
$\text{ZnL}_2\text{-CF}_3^{++}$		

SCHEME 3

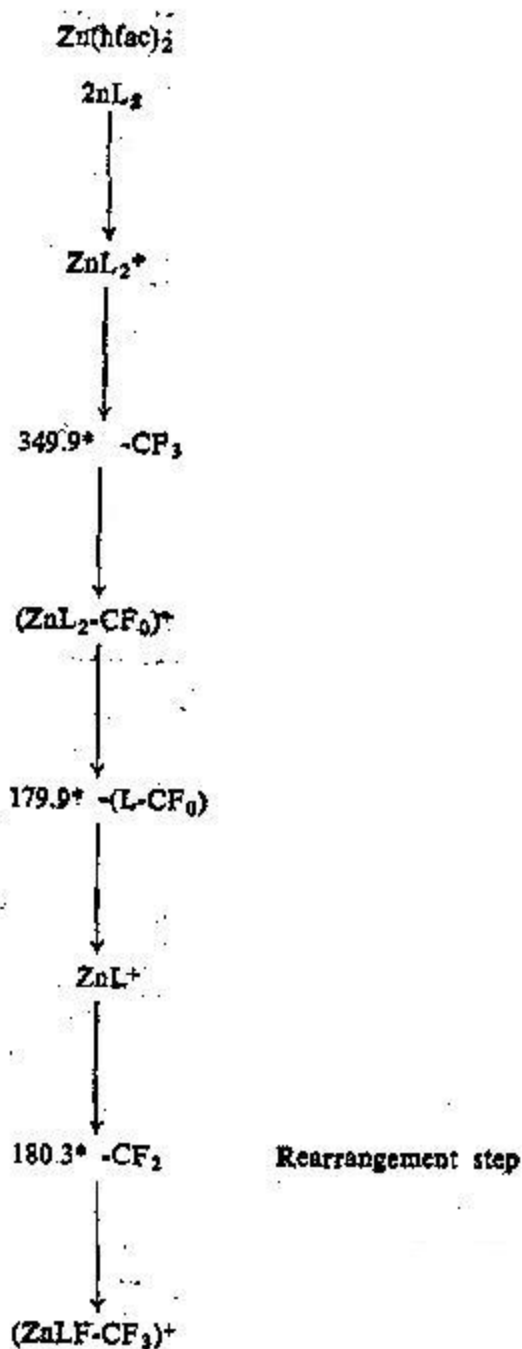


TABLE 4

Mn(hfac)₂

Fragment	m/e	R.P.H.
MnL ₂ ⁺	469	37.3
MnL ₂ -CF ₃ ⁺	400	41.9
MnL ₂ -2CF ₃	331	1.3
MnS ⁺	262	28.1
MnLF-CF ₃ ⁺	212	100
LH-CF ₃	139	34.34
CF ₃ ⁺	69	192.8
Doubly charged ions		
MnL ₂ ⁺⁺	234.5	
MnL ₃ -E ⁺⁺	328.5	

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