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Mass Spectrometric Studies of Metal Acetylacetonates

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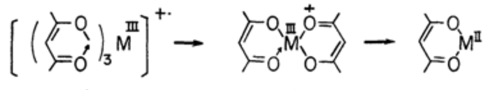
The mass spectra of fifteen metal acetylacetonates measured under the electron impact with 70 eV energies are reported. The acetylacetonates can be divided into three groups, A, B, and C, according to their stability in mass spectrometeric measurements. When the electronegativity of the central metal atom is 1.5—1.6, the complexes show abundant molecular ion peaks (group A); when the electronegativity is 1.6—1.8, no molecular ion appears and the M-L cations show as the highest mass (group B); when the electronegativity is greater than 1.8, there are no peaks arising from fragments containing the metal, only acetylacetone peaks being apparent (group C). Furthermore, the mass spectra of hexafluoroacetylacetone and its copper complex were also measured.

Not much is known about the mass spectrometric fragmentation of organometallic compounds. That is, besides the organometallic carbonyls¹⁾ and ferrocenes,²⁾ which have been studied systematically to some extent, only a few measurements have been carried out on special metal complexes.³⁻⁶⁾ Shannon and Swan³⁾ have, however, investigated iron(III) and aluminum acetylacetonates and have observed that, under electron impact, both compounds lose one ligand; in the case of the ion complex, one more ligand is lost.

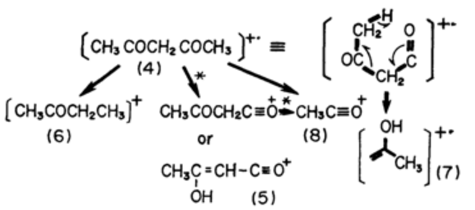


(1) (2) (3)

Metal	*m/e*	*m/e*	*m/e*
Fe:	353(19%)	254(100%)	155(40%)
Al:	324(10%)	225(100%)	126(0%)

Chart 1. Mass fragmentation of Fe(acac)$_3$ and Al(acac)$_3$ (from Ref. 3)

The behavior of fifteen metal acetylacetonates under electron (70 eV) impact will be reported in this communication. The infrared spectrum of acetylacetone in the gaseous state consists of only one strong band, at 1630 cm^{-1}, in the carbonyl-stretching region; therfore, it can be regarded as existing entirely in the enolic form,⁷⁾ although this is not necessarily true under conditions of electron impact.



Cation		Acetylacetone, (rel. int.)
(4)	M⁺	*m/e* 100 (30)
(5)	(M-CH$_3$)⁺	85 (41)
(6)	(M-CO)⁺	72 (3)
(7)	(M-CH$_2$CO)⁺	58 (2)
(8)	CH$_3$C≡O⁺	43(100)

Cation		Dueterated acetylacetone (rel. int.)		
(4)	M⁺	*m/e* 100(5)	101(12)	102(12)
(5)	(M-CH$_3$)⁺	85(6)	86(19)	87(18)
(6)	(M-CO)⁺	72(0)	73(2)	74(2)
(7)	(M-CH$_2$CO)⁺	58(1)	59(2.5)	60(2.0)
(8)	CH$_3$C≡O⁺	43(100)		

Chart 2. Mass fragmentations of acetylacetone and Deuterated Acetylacetone.

Transitions marked with * are supported by the presence of meta-stable ions.

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1) N. Maoz, A. Mandelbaum and M. Cais, *Tetrahedron Letters*, **25**, 2087 (1965).

2) R. E. Winters and R. W. Kiser, *J. Organometal. Chem.*, **4**, 190 (1965); M. Cais and A. Mandelbaum, *Tetrahedron Letters*, **51**, 3847 (1964); L. Friedman, A. P. Irsa and G. Wilkinson, *J. Am. Chem. Soc.*, **77**, 3689 (1965).

3) J. S. Shannon and J. M. Swan, *Chem. Commun.*, **3**, 33 (1965).

4) G. Wilkinson, H. H. Hoehn, L. Pratt and K. F. Watterson, *J. Chem. Soc.*, **1961**, 2738.

5) S. H. H. Chaston, S. E. Livingstone, J. S. Shannon and T. N. Lockyer, *Aust. J. Chem.*, **18**, 1539 (1965).

6) F. Johnson and R. S. Gohlke, *Tetrahedron Letters*, **26**, 1291 (1962).

7) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco (1962), p. 65.

TABLE 1. MASS FRAGMENTATIONS OF METAL ACETYLACETONATES BELONGING TO GROUPS A, B AND C
Relative intensity % of the base peak are enclosed in parentheses. L: ligand.

Group A

	M$^+$	M-15	M-42	M-43	M-L	M-L-15	M-L-42	M-L-43	M-2L
Be(acac)$_2$	207(42.5)	192(100)	165(4)	—	108(78)	—	66(14)	65(1)	—
Al(acac)$_3$	324(18)	—	—	281(1)	225(100)	210(1)	183(7)	182(2)	126(9)
Co(acac)$_2$	257(75)	242(80)	215(1.5)	—	158(100)	—	116(1)	115(6)	59(12)
VO(acac)$_2$	265(89)	250(31)	223(15)	—	166(100)	151(10)	124(5)	123(13)	67(13)
^{64}Zn(acac)$_2$	262(8)	247(11)	220(1)	—	163(12)	148(2)	—	—	64(1)
Pt(acac)$_2$	392(8)	—	—	349(1)	293(3)	278(1)	251(2)	250(1)	—
	393(9)	—	—	350(1)	294(2)	279(2)	252(1)	251(2)	—
	394(7)	—	—	351(1)	295(2)	280(2)	253(1)	252(2)	—

Group B

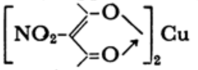
	M$^+$	M-L	M-2L	M-2L-15	M-3L	*m/e*100	*m/e*85	*m/e*43
Co(acac)$_3$	—	257(24)	158(40)	143(5)	59(7)	(28)	(40)	(100)
^{56}Fe(acac)$_3$	—	254(70)	155(86)	—	56(10)	(82)	(92)	(100)
^{52}Cr(acac)$_3$	—	250(100)	151(41)	136(3)	—	(2.5)	(3)	(17.5)

Group C

	M$^+$	M-L	M-2L				*m/e*100	*m/e*85	*m/e*43
Ni(acac)$_2$	—	—	—				(22)	(32)	(80)
MoO$_2$(acac)$_2$	—	—	—				(28)	(42)	(100)
Pd(acac)$_2$	—	—	—				(13.5)	(19)	(100)
Cu(acac)$_2$	—	—	—				(68)	(87)	(100)
Cu(acac-NO$_2$)$_2$	—	—	—	[acac-NO$_2$] 145(1)			(10)	(14)	(100)
Pd(acac-Br)$_2$	—	—	—	[acac-Br] 180(2.5) 178(2.5)	[acac-Br]-CH$_3$ 165(4) 163(4)	[acac-Br]-CH$_2$CO 138(5) 136(5)	(8)	(10)	(100)

Base peaks of Zn(acac)$_2$ and Pt(acac)$_2$ appear at *m/e* 43.
Base peak of Ni(acac)$_2$ appears at *m/e* 28.

Cu(acac-NO$_2$)$_2$:



Pd(acac-Br)$_2$:

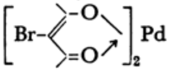


TABLE 2. METASTABLE ION PEAKS OF METAL ACETYLACETONATES BELONGING TO GROUP A

	Al(acac)$_3$	Be(acac)$_2$	Co(acac)$_2$	VO(acac)$_2$	Pt(acac)$_2$
			m/e		
M→M-L	156	56(a)	—	103	—
M→M-15	—	178(b)	227	235	—
M→M-42	—	131(c)	—	187	—
M-15→M-L	—	60(d)	103	110	—
M-L→M-L-42	148	40(e)	—	—	—

The mass spectrum of acetylacetone itself is simple, consisting of the peaks tabulated in Chart 2. When acetylacetone was vaporized in the inlet system together with D$_2$O, all peaks except that at *m/e* 43 were shifted 1 or 2 mass units higher; therefore, peaks 4 through 7 all contain the active methylene group (or its enolic counterpart). The peaks can thus be assigned as is shown in Chart 2. Peak 6, due to the loss of CO, corresponds to a rearrangement which has previously been noted in simple ketones and esters[8] and in some π-bonded organometallic compounds such as ferrocenes,[1] whereas the weak cation, 7, can be assigned to

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[8] J. H. Bowie, R. Grigg, D. H. Williams, S. O. Lawesson and G. Schroll, *Chem. Commun.*, **17**, 403 (1965).

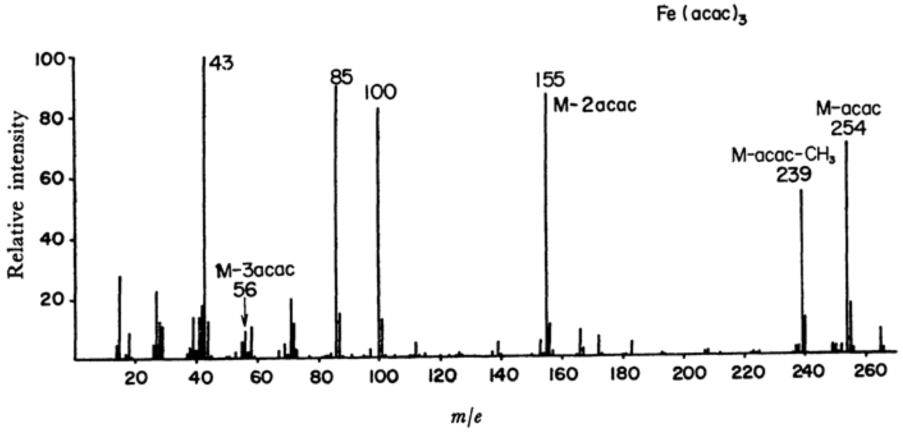

Fig. 1. Mass spectrum of Fe(acac)$_3$.

an enol ion of acetone formed by a McLafferty rearrangement.[9]

The present study has revealed that the metal acetylacetonates can be divided into three groups, A, B, and C, according to their stability in mass spectrometric measurements, and that the smaller the electronegativity of the metal, the more stable the complex; furthermore, the introduction of electron-attracting groups into the ligand also enhances the stability.

Group A. Complexes that afford molecular ion, M^+, peaks:
Be(acac)$_2$, Al(acac)$_3$, Co(acac)$_2$, VO(acac)$_2$ Pt(acac)$_2$, and Zn(acac)$_2$.

As is summarized in Table 1, all peaks are accounted for by the M^+ cation and peaks due to the loss of methyl, ketene, acetyl, and ligand, L, radicals.

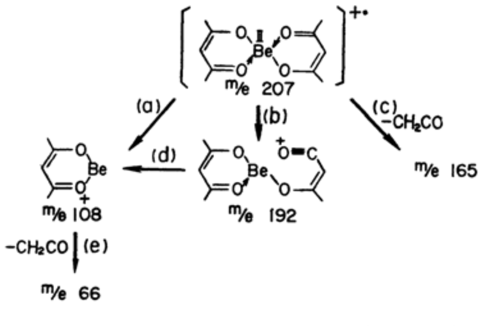

Chart 3. Mass fragmentations of Be(acac)$_2$

TABLE 3. PEAKS OF DEUTERATED Al(acac)$_3$

m/e (Rel. Int.) Al(acac)$_3$	Deuterated Al(acac)$_3$ m/e (Rel. Int.)			
324(18)	324(4),	325(5),	326(3),	327(1)
225(100)	225(41),	226(100),	227(72)	
141(38)	141(10),	142(11)		
126(9)	126(4),	127(5)		

Peaks at m/e 100, 85 and 43 are observed in the low mass region; it is obvious that these arise from the acetylacetone moiety. The metastable ion peaks are tabulated in Table 2; in Chart 3 the fragmentation of beryllium acetylacetonate, which shows the largest number of metastable ion peaks, is depicted. Interestingly, the vaporization of aluminum acetylacetonate with D_2O in the inlet system resulted in the incorporation of three, two, and one deuterium atoms, respectively, in the cations containing three ligands, two ligands and one ligand (Table 3); the deuteration presumably proceeds by the following route, in which the valency of the metal is transiently reduced from three to two, with the concomitant ketonization of the ligand.

Group B. Complexes that lack the M^+ peak and which show the M-L cation as the peak with the highest mass: Co(acac)$_3$, Fe(acac)$_3$ and Cr(acac)$_3$. It may be seen that the central metal in the undissociated complex is tervalent in all three compounds. The spectrum of iron(III) acetylacetonate is shown in Fig. 1 (the spectra of the other two complexes are similar). As Chart 1 shows, the mass spectra of iron(III) and aluminum acetylacetonates have already been measured,[3] but the relative peak intensities differ considerably from the present measurements (the relative intensity is enclosed in parentheses):

Present Measurements of iron(III) and aluminum acetylacetonates (cf. Table 1)
Fe(acac)$_3$ M^+ 353(0); M-L 254 (70);
M-2L 155(86)
Al(acac)$_3$ M^+ 324(18); M-L 225(100);
M-2L 126(9)

This illustrates the sensitivity of the acetylacetonates towards experimental conditions, but both series of measurements indicate that the iron(III) acetylacetonate undergoes a loss of two ligand radicals more readily than does aluminum acetylacetonate, behavior that has been attributed to the relative readiness of the iron atom to assume a bivalent

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[9] F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

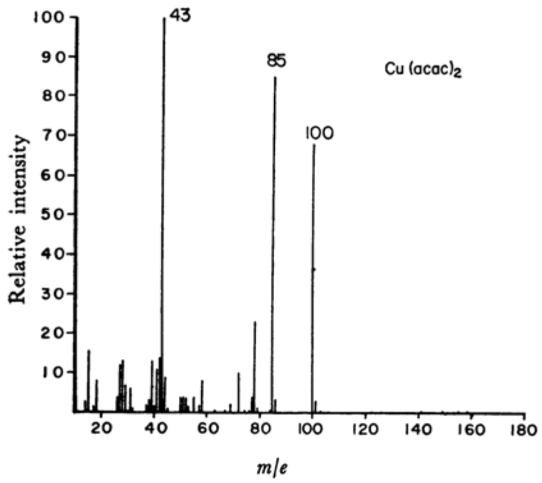

Fig. 2. Mass spectrum of Cu(acac)$_2$.

TABLE 4. RELATION BETWEEN ELECTRONEGATIVITY OF METALS AND CLASSIFICATION OF METAL ACETYLACETONATES

Metal	Electronegativity11)	Classification
Be	1.5	A
Al	1.5	A
V	1.6	A
Zn	1.6	A
Cr	1.6	B
Co	1.8	B
Fe	1.8	B
Ni	1.8	C
Mo	1.8	C
Cu	1.9	C
Pt	2.2	A
Pd	2.2	C

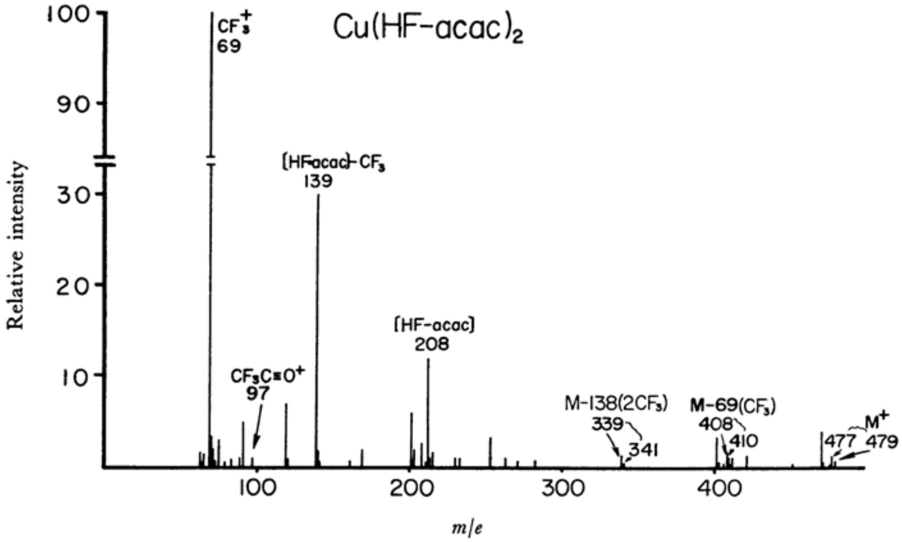

Fig. 3. Mass spectrum of Cu(HF-acac)$_2$.

form (Chart 1)3).

Group C. Complexes that show peaks due only to acetylacetone:

Cu(acac)$_2$, Cu($CH_3COCHNO_2COCH_3$)$_2$,
Pd($CH_3COCHBrCOCH_3$)$_2$, MoO_2(acac)$_2$,
and Ni(acac)$_2$.

That is the spectra of these complexes show no peaks that arise from fragments containing the metal; the spectra are very similar to that of acetylacetone itself (Fig. 2). It should be noted that, although Cu(acac)$_2$ is very stable and can be purified by distillation, it is readily decomposed under electron impact.

It is known that the stability of a complex increases with a decrease in the electronegativity of the central metal.10) This general trend seems to hold for their behavior under electron impact as well. That is as is indicated in Table 4, complexes in which the electronegativity of the central metal is 1.5—1.6 give abundant molecular ion peaks (group A), those in which the electronegativity is 1.6—1.8 give M-L cations as the peak of highest mass (group B), and those in which it is more than 1.8 afford only acetylacetone peaks. In other words, with one exception, Pt, the smaller the electronegativity of the metal, the stabler the acetylacetonate molecule in the face of electron impact.

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10) D. P. Graddon, "An Introduction to Co-ordination Chemistry," Chapter 4, Pergamon Press Ltd., London (1961).

11) W. Gordy and W. J. O. Thomas, *J. Chem. Phys.*, **24**, 439 (1956).

It is also known that the introduction of electronegative atoms such as halogen into ligands increases the stability of complexes.[12] In accordance with this general trend, the hexafluoroacetylacetonate (HF-acac) of copper was stabilized to the extent that the mass spectrum showed an M^+ peak in contrast to that of $Cu(acac)_2$ which belongs to group C. The fragmentation of hexafluoroacetylacetone is similar to that of acetylacetone, as is substantiated by the fragmentations of its dideuterio derivative (Table 5).

TABLE 5. PEAKS OF HEXAFLUOROACETYLACETONE AND THE DIDEUTERIO DERIVATIVE

Ion	Hexafluoroacetylacetone (HF acac) $CF_3COCH_2COCF_3$		Deuterated HF acac $CF_3COCD_2COCF_3$	
	m/e (Rel. Int.)			
M^+	208(4)	208(2)	209(4)	210(2)
$(M-CF_3)^+$	139(40)	139(40)	140(26)	141(20)
CF_3CO^+	97(2)	97(2)		
CF_3^+	69(100)	69(100)		

The spectrum of copper(II) hexafluoroacetylacetonate is shown in Fig. 3. The fragmentation pattern is quite similar to those of the other complexes of group A in that peaks at M, $M-CF_3$ and M-138 are present; however, they are here present as doublets, in accordance with the isotopic abundance of copper, and the lower-mass region consists of ions due to hexafluoroacetylacetone.

Experimental

Mass spectra were obtained with a Hitachi RMU-6D Mass Spectrometer, with an energy of 70 V and an 80 μ amp. ionizing current. The temperature of the ion source was 250°C. All the samples were synthesized according to known procedures.[13]

Two of the present authors especially (K. N. and S. S.) are grateful to the Toyo Rayon Company, Ltd., for the grant enabling them to purchase the RMU-6D mass spectrometer.

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[12] R. E. Sievers, B. W. Ponder, M. L. Moris and P. W. Moshier, *J. Inorg. Chem.*, **2**, 693 (1963).

[13] $Al(acac)_3$: R. C. Young, *Inorg. Syn.*, **2**, 25 (1946); $Be(acac)_2$: A. Arch and R. C. Young, *ibid.*, **2**, 17 (1946); $VO(acac)_2$: B. E. Bryant and W. C. Fernelius, *ibid.*, **5**, 115 (1957); $MoO_2(acac)_2$: W. C. Fernelius and K. Terada, *ibid.*, **6**, 147 (1960); $Cr(acac)_3$: W. C. Fernelius and J. E. Blanch, *ibid.*, **5**, 130 (1957); $Pt(acac)_2$: A. Werner, *Ber.*, **34**, 2583 (1901); $Fe(acac)_3$, $Co(acac)_2$, $Ni(acac)_2$: R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958); $Co(acac)_2$: B. E. Bryant and W. C. Fernelius, *Inorg. Syn.*, **5**, 188 (1957).; $Cu(acac)_2$: O. E. Denoon Jr., "Org. Syntheses," Coll. Vol. III, 16, (1958); $Cu[C_5H_6O_2(NO_2)]_2$: J. P. Collman, R. L. Marshall, W. L. Young and S. D. Goldby, *J. Inorg. Chem.*, **1**, 704 (1962); $Pd(acac)_2$: A. A. Grinberg and I. K. Simonova, *Zhur. Pukad. Khim.*, **26**, 880 (1953); $Pd(C_5H_6O_2Br)_2$: A. Kasahara, K. Ujiie and K. Tanaka, This Bulletin, in press; $Cu(C_5HO_2F_6)_2$: M. L. Moris and R. W. Moshier, *J. Inorg. Chem.*, **2**, 411 (1963).