Inorganica Chimica Acta, 22 (1977) 101–105

Mass Spectra of Tris(β-diketonato)gallium(III) and -indium(III)

J. CHARALAMBOUS, R. G. GOSSETT, M. H. JOHRI and M. J. KENSETT

Department of Chemistry, The Polytechnic of North London, Holloway, London N7 8DB, U.K.

Received August 12, 1976

The mass spectra of the gallium(III) and indium (III) complexes M(acac)$_3$ (acacH = acetylacetone) and M(tfac)$_3$ (tfacH = trifluoroacetylacetone) have been investigated. The main decomposition pathways of the complexes M(acac)$_3$ involve mainly loss of ligand radicals from the molecular ion [M(acac)$_3$]$^+$ and lead to the ions [M(acac)$_2$]$^+$, [M(acac)]$^+$ and [M]$^+$. The formation of the ions [M(acac)]$^+$ and [M]$^+$, and the fragmentation behaviour of [M(acac)]$^+$ are rationalized in terms of the stability of oxidation state +I of gallium and indium. The complexes also exhibit reactions involving elimination of ligand fragments, such as $CH_3^\bullet$, H_2O, CH_2CO and CH_3CO-$CHCO$. The molecular ion [M(tfac)$_3$]$^+$ of each of the complexes derived from trifluoroacetylacetone fragments mainly by ligand radical elimination to give the ion [M(tfac)$_2$]$^+$ whose subsequent fragmentation proceeds via *reactions involving loss of ligand fragments.*

Introduction

The mass spectra of several main group and transition metal β-diketonates have been extensively studied [1–4]. Differences in the fragmentation behaviour between main group metal β-diketonates and transition metal β-diketonates have been interpreted in terms of the ability of transition metal to change oxidation state [5]. This paper presents and discusses the mass spectra of the gallium(III) and indium(III) β-diketonates M(acac)$_3$ (acacH = acetylacetone) and M(tfac)$_3$ (tfacH = tifluoroacetylacetone). Emphasis is given on the question of how the fragmentation course is affected as a result of the presence of a metal which exhibits two oxidation states separated by two units and on comparison with the fragmentation behaviour of other metal β-diketonates.

Experimental

The complexes M(acac)$_3$ (M = Ga or In) were prepared as described in the literature [6]. Ga(tfac)$_3$ (Found: C, 34.3; H, 2.3. $C_{15}H_{12}F_9GaO_6$ requires: C, 34.1; H, 2.3%) and In(tfac)$_3$ (Found: C, 31.2; H, 2.0. $C_{15}H_{12}F_9InO_6$ requires: C, 31.3; H, 2.1%) were prepared in a similar manner (*ca.* 40% yield) and were purified by repeated sublimation at 100 °C/0.1 mm. The mass spectra were obtained on a Hitachi RMS–4 spectrometer operating at 80 eV and by use of a direct insertion probe at *ca.* 100 °C. Exact mass measurements and enhanced metastable spectra were obtained on an AEI MS–9 instrument at the Physico-Chemical Measurements Unit, Harwell.

Results and Discussion

The mass spectra of the compounds studied are given in Tables I to VI. Only the metal-containing ions are recorded; these were easily identified because of the isotope pattern due to the naturally occurring isotopes of the metal (^{69}Ga 60.4, ^{71}Ga 39.6, ^{113}In 4.3, ^{115}In 95.7%). The spectra also showed the presence of non-metal species arising from the ligands; the sum of the intensities of these ions was less than 15% of the total ion current.

M(acac)$_3$ Complexes

The fragmentation pattern of the M(acac)$_3$ (M = Ga or In) complexes is given in Scheme 1. Both the gallium and indium compounds give a molecular ion [M(acac)$_3$]$^+$ which fragments mainly by loss of a ligand radical to give the ion [M(acac)$_2$]$^+$. This ion is present as the most intense ion in both cases and fragments both by loss of odd- and even-electron species. In this respect the behaviour of the gallium and indium compounds resembles that of transition metal trisacetylacetonates [1]. However, whereas in the case of the transition metal compounds the ion [M(acac)$_2$]$^+$ shows loss of acac$^\bullet$ as well as loss of $CH_3^\bullet$ radicals, the ion [M(acac)$_2$]$^+$ (M = Ga or In) shows only loss of acac$^\bullet$ to give the ion [M(acac)]$^+$. For the transition metal compounds the loss of a radical from the even-electron ion [M(acac)$_2$]$^+$ has been rationalised in terms of reduction of the metal to its +II oxidation state. As we have suggested earlier for

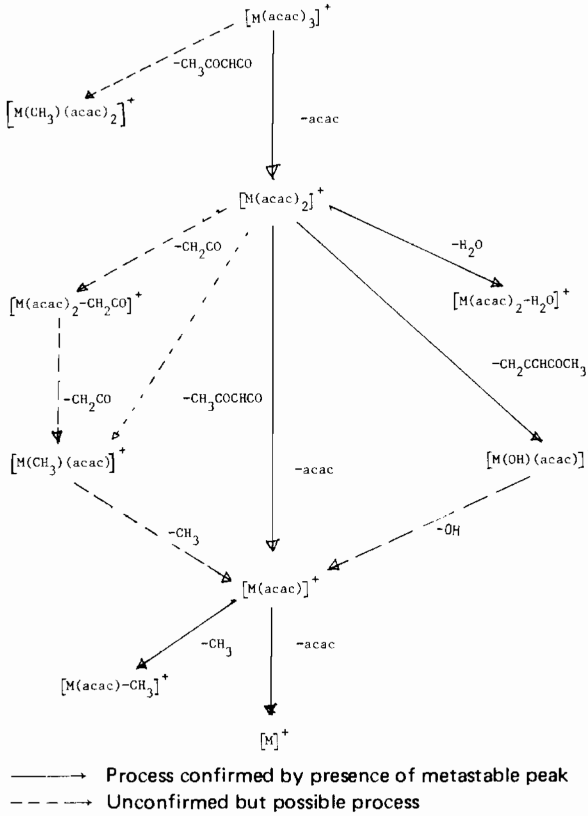
---

[a] In this paper the odd- or even-electron character of an ion is indicated only when the oxidation state of the metal in the ion is specified.

TABLE I. Ion Abundances[a] for $M(acac)_3$.

Ion[b]	M in $M(acac)_3$	
	Ga m/e[c]	In m/e
$[M(acac)_3]^+$	366 2	412 8
$[M(acac)_3 - CH_3COCHCO]^+$	282 0.5	327 0.5
$[M(acac)_2]^+$	267 81	313 63
$[M(acac)_2 - H_2O]^+$	249 0.2	295 0.3
$[M(acac)_2 - CHO]^+$	209 3	–
$[M(acac)_2 - CH_2CO]^+$	–	270 1
$[M(acac)_2 - CO_2]^+$	–	269 1
$[M(acac)_2 - CH_2O_2]^+$	–	267 1
$[M(acac)_2 - CH_2CCHCOCH_3]^+$	185 7	231 1
$[M(acac)_2 - CH_3COCHCO]^+$	183 3	–
$[M(acac)]^+$	168 1	214 6
$[M(acac) - CH_3]^+$	153 2	199 3
$[M(acac) - CHO]^+$	–	185 0.2
$[M(acac) - CH_2O_2]^+$	–	158 0.2
$[M]^+$	69 2	115 13

[a] Abundances are expressed as percentage of the total ion current due to metal-containing ions. All species are corrected for isotopic abundance. [b] Only metal-containing ions are recorded. [c] m/e values are given for the ions containing ^{69}Ga and ^{115}In.



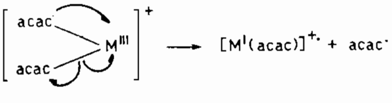
Scheme 1. Fragmentation Scheme for $M(acac)_3$.

TABLE II. Metastable Ions in $M(acac)_3$.

Transition	M in $M(acac)_3$	m/e Values for Transition[a]		m*	
				Found	Calcd
$[M(acac)_3 - acac]^+ \longrightarrow [M(acac)_2]^+$	Ga	366	267	195.0	194.7
	In	412	313	238.0	237.8
$[M(acac)_2]^+ \longrightarrow [M(acac)_2 - H_2O]^+$	In	313	295	279.0	278.4
$[M(acac)_2]^+ \longrightarrow [M(acac)_2 - CH_3CH_2CHO]$	Ga	267	209	163.0	163.6
$[M(acac)_2]^+ \longrightarrow [M(acac)_2 - CH_2CCHCOCH_3]^+$	Ga	267	185	128.0	128.2
	In	313	231	171.0	170.6
$[M(acac)_2]^+ \longrightarrow [M(acac)_2 - CH_3COCHCO]^+$	Ga	267	183	125.5	125.4
$[M(acac)_2 - acac]^+ \longrightarrow [M(acac)]^+$	Ga	267	168	106.0	105.7
	In	313	214	146.0	146.3
$[M(acac)_2 - CH_2CCHCOCH_3 - OH]^+ \longrightarrow [M(acac)]^+$	Ga	185	168	153.0	152.5
$[M(acac)]^+ \longrightarrow [M(acac) - CH_3]^+$	Ga	168	153	139 0	139.3
	In	214	199	185.0	185.1
$[M(acac)]^+ \longrightarrow [M]$	In	214	115	62.0	61.8

[a] Only transitions involving ^{69}Ga and ^{115}In are given.

analogous systems [7], the loss of acac$^\cdot$ from $[M(acac)_2]^+$ (M = Ga or In) can be correlated with the stability of oxidation state +I by assuming that the loss is accompanied by transfer of one electron from the remaining ligand to the metal.



On this basis the daughter ion $[M(acac)]^+$ is an odd-electron ion with the metal in its +I oxidation state.

TABLE III. Accurate Mass Measurements on Selected Peaks for $M(acac)_3$.

Compound	Nominal Mass	Determined Mass	Ion Assignment	Calculated Mass
$Ga(acac)_3$	366	366.0608	$C_{15}H_{21}O_6{}^{69}Ga$	366.0593
	209	208.9738	$C_7H_8O_3{}^{69}Ga$	208.9728
	153	152.9467	$C_4H_4O_2{}^{69}Ga$	152.9466
$In(acac)_3$	412	412.0364	$C_{15}H_{21}O_6{}^{115}In$	412.0377
	255	254.9525	$C_7H_8O_3{}^{115}In$	254.9513
	231	230.9514	$C_5H_8O_3{}^{115}In$	230.9513
	229	228.9711	$C_6H_{10}O_2{}^{115}In$	228.9720
	199	198.9253	$C_4H_4O_2{}^{115}In$	198.9249

TABLE IV. Ion Abundances[a] for $M(tfac)_3$.

Ion[b]	M in $M(tfac)_3$			
	Ga m/e[c]		In m/e	
$[M(tfac)_3]^+$	528	4	574	10
$[M(tfac)_3 - F]^+$	509	2	555	0.2
$[M(tfac)_3 - CH_2CO - F]^+$	–		513	0.2
$[M(tfac)_3 - CF_3]^+$	459	0.2	505	0.6
$[M(tfac)_3 - CH_2CO - F - HF]^+$	447	1	493	2
$[M(tfac)_2]^+$	375	37	421	50
$[M(tfac)_2 - H_2O]^+$	357	2	403	0.5
$[M(tfac)_2 - F]^+$	–		402	0.5
$[M(tfac)_2 - CO]^+$	347	1	393	1
$[M(tfac)_2 - CF_2]^+$	325	20	371	7
$[M(tfac)_2 - CF_3]^+$	306	0.6	–	
$[M(tfac) - CF_2 - HF]^+$	305	0.5	351	3
$[M(tfac)_2 - CF_2 - HF - CH_2CO]^+$	263	0.4	309	7
$[M(tfac) + F]^+$	241	4	287	2
$[M(tfac)]^+$	222	1	268	1
$[M(tfac)_2 - CF_2 - HF - CH_2CO - CF_2]^+$	213	2	259	0.7
$[M(tfac) - CH_3]^+$	–		253	0.2
$[M(tfac) - F]^+$	–		239	0.4
$[M(tfac)F - CF_2]^+$	191	3	237	0.5
$[M]^+$	69	4	115	8

[a] Abundances are expressed as percentage of the total ion current due to metal-containing ions. All species are corrected for isotopic abundance. [b] Only metal-containing ions are recorded. [c] m/e values are given for the ions containing ${}^{69}Ga$ and ${}^{115}In$.

Significantly, the further decomposition of $[M(acac)]^+$ involves mainly metastable-supported elimination of radicals ($acac^•$ and $CH_3^•$) thus providing some support for the suggestion. The importance of the +I oxidation state in affecting the fragmentation pattern of the gallium and indium compounds is also indicated by the absence of bare metal ions and the very low abundance of $[M(acac)]^+$ in the spectra of the aluminium and scandium trisacetylacetonates [1], two metals for which the +I oxidation state is not normally available. In close similarity to results obtained for several other acetylacetonates the ion $[M(acac)_2]^+$ (M = Ga or In) shows loss of the even-electron species H_2O, CH_2CO and $CH_3COCHCH_2$. The reactions are often metastable-supported. In addition when M = Ga or In the ions $[M(acac)_2]^+$ show a variety of weak reactions involving elimination of the even-electron species CHO, CO_2, CH_2O_2 and $CH_3COCHCO$ which have not been observed in the spectra of other trisacetylacetonates. The loss of the species $CH_3COCHCO$ from $[M(acac)_2]^+$ is pronounced and interesting. This reaction, occurring only when M = Ga, is metastable supported and may result in the formation of a metal–methyl species by migration of the methyl group. An analogous reaction of the ion $[M(acac)_3]^+$ is shown by both the gallium and indium compounds but in these cases the abundance of the daughter ion is low. Methyl migration to the metal has not been observed in the spectra of other acetylacetonates but phenyl migration is common in the spectra of dibenzoylmethanates [1].

$M(tfac)_3$ Complexes

The fragmentation pattern of the $M(tfac)_3$ (M = Ga or In) complexes is characterised by a high degree of ligand fragmentation. Both complexes give a molecular ion $[M(tfac)_3]^+$ which fragments mainly by loss of a ligand radical to give the ion $[M(tfac)_2]^+$. In addition the molecular ions show a variety of reactions involving elimination of the ligand fragments $F^•$, $CH_3^•$, HF and CH_2CO. Apart from loss of the even-electron species CH_2CO, which is shown by the molecular ions of $M(tfac)_3$ (M = Cr, Fe or Co), these ligand fragmentation reactions are not shown by the molecular ions of other $M(tfac)_3$ complexes [1]. The decomposition of the ion $[M(tfac)_2]^+$ also involves reactions which have not been observed in the spectra of other $M(tfac)_3$ complexes. The reaction sequence $[M(tfac)_2]^+ \xrightarrow{*} [M(tfac)_2 - CF_2]^+ \xrightarrow{*} [M(tfac)_2 - CF_2 - HF]^+ \xrightarrow{*} [M(tfac)_2 - CF_2 - HF - CH_2CO]^+ \longrightarrow [M(tfac)_2 - CF_2 - HF - CH_2CO - CF_2]^+$ is prominent in the

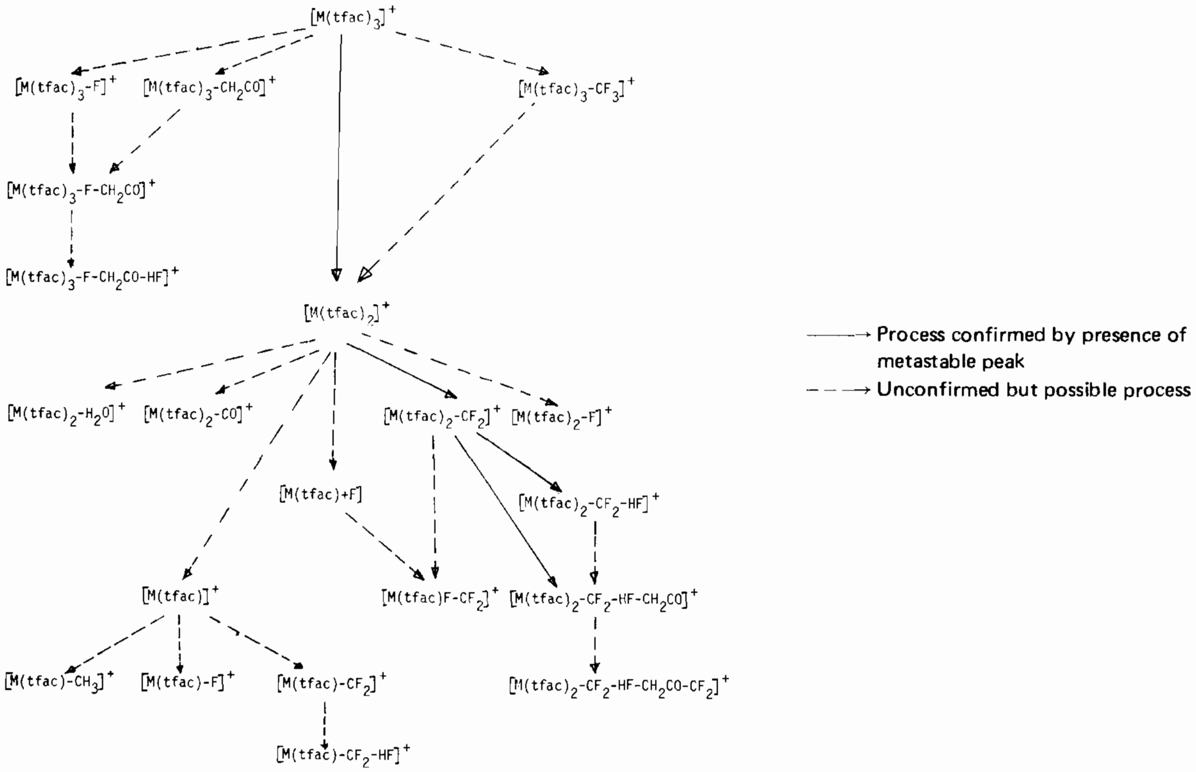
TABLE V. Metastable Ions in $M(tfac)_3$.

Transition	M in $M(tfac)_3$	m/e Values for Transition[a]		m*	
				Found	Calcd
$[M(tfac)_3 - tfac]^+ \longrightarrow [M(tfac)_2]^+$	Ga	528	375	266	266.33
	In	574	421	309	308.78
$[M(tfac)_2]^+ \longrightarrow [M(tfac)_2 - CF_2]^+$	Ga	375	325	282	281.66
	In	421	371	327	326.93
$[M(tfac)_2 - CF_2]^+ \longrightarrow [M(tfac)_2 - CF_2 - HF]^+$	In	371	351	332	332.07
$[M(tfac)_2 - CF_2]^+ \longrightarrow [M(tfac)_2 - CF_2 - HF - CH_2CO]^+$	Ga	325	263	212.5	212.82
	In	371	309	257	257.36

[a] Only transitions involving ^{69}Ga and ^{115}In are given.

TABLE VI. Accurate Mass Measurements on Selected Peaks for $M(tfac)_3$.

Compound	Nominal Mass	Determined Mass	Ion Assignment	Calculated Mass
$Ga(tfac)_3$	528	527.9747	$C_{15}H_{12}O_6F_9{}^{69}Ga$	527.9744
	325	324.9615	$C_9H_8O_4F_4{}^{69}Ga$	324.9617
	263	262.9448	$C_7H_5O_3F_3{}^{69}Ga$	262.9445
	240	240.9411	$C_5H_4O_2F_4{}^{69}Ga$	240.9402
	191	190.9442	$C_4H_4O_2F_2{}^{69}Ga$	190.9434
$In(tfac)_3$	574	573.9538	$C_{15}H_{12}O_6F_9{}^{115}In$	573.9529
	421	420.9364	$C_{10}H_8O_4F_6{}^{115}In$	420.9365
	371	370.9388	$C_9H_8O_4F_4{}^{115}In$	370.9397
	268	267.9213	$C_5H_4O_2F_3{}^{115}In$	267.9202



Scheme 2. Fragmentation Scheme for $M(tfac)_3$.

spectra of both compounds. The first two steps of this sequence have been observed in the spectra of other tristrifluoroacetylacetonates but the subsequent losses of CH_2CO and CF_2 have not. Other reactions which are shown by $[M(tfac)_2]^+$ when M = Ga or In only are the loss of the even-electron species H_2O and CO.

Both the gallium and indium compounds show the ions $[M(tfac)F]^+$ and $[M(tfac)F - CF_2]^+$. The presence of these ions suggests migration of fluorine to the metal. In this respect the behaviour of $M(tfac)_2$ (M = Ga or In) resembles that of other trifluoroacetylacetonates. However whereas such complexes often exhibit loss of neutral metal fluorides the gallium and indium complexes do not.

The ions $[M(tfac)]^+$ and $[M]^+$ are present in the spectra of both compounds. The abundance of the former ion is low but the ion $[M]^+$ is fairly abundant especially when M = In. The presence of $[M]^+$ contrasts the absence of bare metal ions in the spectra of $M(tfac)_3$ (M = Al, Cr, Fe or Co) and reflects the stability of oxidation state +I of gallium and indium.

Acknowledgments

We are grateful to the Science Research Council and Physico-chemical Measurements Unit for facilities. We also thank Mr D. V. Diggins for obtaining some of the spectra.

References

1 J. B. Westmore, in J. Charalambous (ed.), "Mass Spectrometry of Metal Compounds", Butterworths, London (1975); Chapter 9 and references therein.

2 P. F. R. Ewings, P. G. Harrison and D. E. Fenton, *J. Chem. Soc. Dalton*, 821 (1975).

3 M. Das and S. E. Livingstone, *Aust. J. Chem., 27,* 1177 (1974).

4 K. D. Haegele, V. Schurig and D. M. Desiderio, *Inorg. Chem., 13,* 1960 (1974).

5 M. J. Lacey and J. S. Shannon, *Org. Mass Spectrometry, 6,* 931 (1972).

6 G. T Morgan and H. D. K Drew, *J. Chem. Soc., 119,* 1058 (1921).

7 J. Charalambous, *Inorg. Chim. Acta, 18,* 241 (1976).