Influence of the Change of the Oxidation State of the Rare Earths upon their Mass Fragmentation in Acetylacetonate Complexes

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Abstract

A change of the oxidation state of rare earths upon their mass fragmentation in acetylacetonate complexes has been proved. Ce^{III} and Gd^{III} acac complexes preserved the original oxidation state whereas the complexes with Sm^{III}, Eu^{III} and Yb^{III} changed their oxidation state (III → II). In both cases different fragmentation pathways have been detected.

Introduction

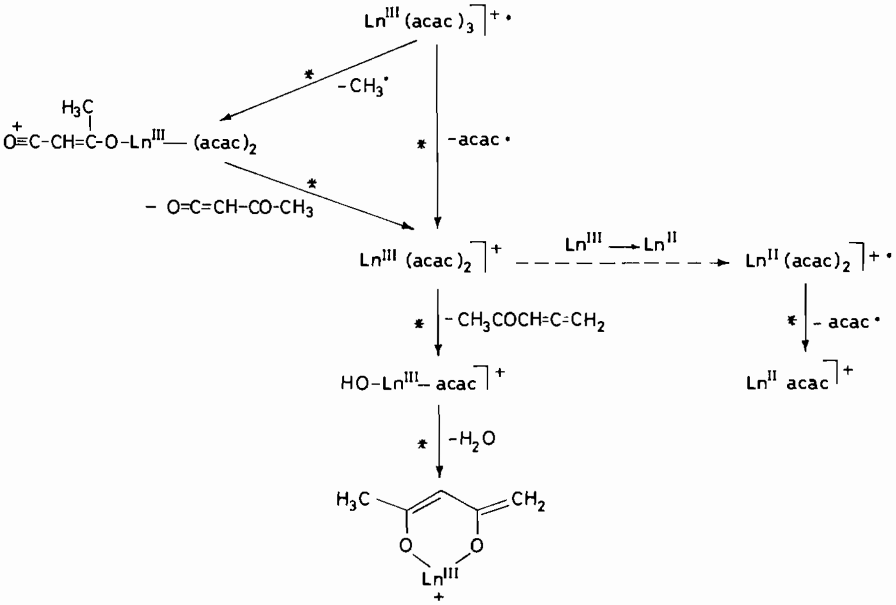
The rare earth cations occur mostly in an oxidation state of III, sometimes of II or IV. In acetylacetonate (acac) complexes they exist solely as tripositive ions. Many of the above complexes have been examined using mass spectrometry [1–7], especially with acac derivatives such as trifluoroacetylacetone [3], hexafluoroacetylacetone [4], thenoyltrifluoroacetone [5], benzoyltrifluoroacetone [6] or pivaloyltrifluoroacetone [7].

During mass fragmentation of acac complexes, a number of metal cations may preserve the original oxidation state or change it [8, 9]. This has a direct influence on the fragmentation process.

In the course of our investigation on yttrium, lanthanum and lanthanide (except promethium) acac complexes, three types of mass fragmentation have been observed: (i) fragmentation with preservation of the original oxidation state of the rare earth, (ii) fragmentation during which the central cation of the complex changed its valency (III → II), and (iii) mixed fragmentation in which both above processes occurred simultaneously.

Experimental

Low resolution mass spectra were recorded on a double focussing mass spectrometer JMS D-100 made



Scheme 1. Fragmentation pathways observed in $Ln^{III}(acac)_3$ complexes.

TABLE 1. Electron Impact Mass Spectra of Ln(acac)$_3$ Complexes[a]

Ln	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
$Ln^{III}(acac)_3]^{+\cdot}$	386(37)	436(28)	437(44)	438(31)	439(28)	449(33)	450(30)	455(26)	456(40)	461(35)	462(39)	463(33)	466(36)	471(26)	472(44)
$Ln^{III}(acac)_2C_4H_4O_2]^+$	371(3)										447(3)	448(3)	451(3)	456(2)	457(6)
$Ln^{III}(acac)_2]^+$ or $Ln^{II}(acac)_2]^{+\cdot}$	287(100)	337(100)	338(100)	339(100)	340(100)	350(100)	351(100)	356(100)	357(100)	362(100)	363(100)	364(100)	367(100)	372(100)	373(100)
$Ln^{III}(acac)OH]^+$	205(10)	255(17)	256(21)	257(19)	258(18)	268(13)		274(15)	275(11)	280(10)	281(10)	282(11)	285(8)	290(5)	291(7)
$Ln^{II}acac]^+$	188(3)	238(2)		240(3)	241(13)	251(22)	252(64)		258(3)	263(8)	264(7)	265(10)	268(16)	273(28)	274(5)
$Ln^{III}C_5H_6O_2]^+$	187(7)	237(9)	238(8)	239(7)	240(10)			256(17)	257(7)		263(9)	264(8)	267(7)		273(7)

[a] The ions with relative abundances less than 2% are omitted. Relative abundances of ions calculated relate to the most abundant isotopes.

by Jeol. High resolution data were obtained on the same instrument using a resolving power of 8000 and peak matching technique. Elemental compositions of the discussed ions were determined with error less than 5 ppm in relation to perfluorokerosene-H. Metastable ions were recorded on a JMS D-100 mass spectrometer equipped with an MS MT-01 metastable ion detector using accelerating voltage within the range of 1500–3000 V.

Compounds were introduced by direct insertion probe in electron impact conditions (75 eV, 300 μA), with an accelerating voltage of 3000 V, a source temperature of 200 °C and an inlet temperature of 40–230 °C.

Synthesis of the Complexes

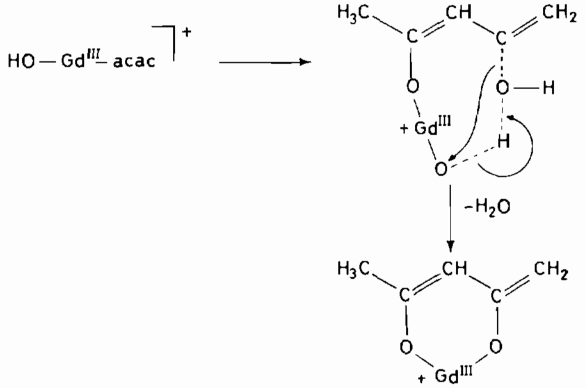
The trihydrate rare earth acetylacetonates, Ln(acac)$_3$·3H$_2$O, were prepared according to the literature [10] and recrystallized from ethanol. Elemental analyses were performed for checking the purity of complexes; the results were in good agreement with expected formulae within 0.4%.

Results and Discussion

Mass spectra of investigated compounds are summarized in Table 1.

The possibility of change of an oxidation state differentiated the individual rare earths and one of the above mentioned types of electron impact induced fragmentation (i–iii) could be ascribed to the complexes with acetylacetone. The differentiation of fragmentation has been observed after the first loss of acetylacetonate radical, leading to the Ln(acac)$_2$ cation, which is the most abundant ion in all the recorded mass spectra. Further decompositions of the above ion have been based on a preservation or a change of primary oxidation state of Ln [8, 9], as shown in Scheme 1.

A double elimination of neutral particles from the $Ln^{III}(acac)_2]^+$ ion, dienone and H$_2$O (= elimination of Hacac in two stages), has been observed for the Gd(acac)$_3$ complex, whereas a loss of acac· from $Ln^{II}(acac)_2]^{+\cdot}$, in agreement with the 'even electron rule' [11], was performed especially in the case of Eu(acac)$_3$. The loss of the acetylacetonate radical depended upon direct cleavage of the metal–ligand bond, whereas a two stage elimination of the acetylacetone molecule proceeded through a double rearrangement. The first elimination of dienone was based on McLafferty's rearrangement [1], whereas for the second one the following scheme has been proposed



Scheme 1. Fragmentation pathways observed in Ln^{III}(acac)$_3$ complexes.

The ions $\mathrm{Ln^{III}C_5H_6O_2]^+}$ and $\mathrm{Ln^{II}acac]^+}$ formed as a result of both the above types of fragmentation differed in the oxidation state of the rare earths, the structure and their elemental compositions. Relative intensities of both types of ion in relation to the central atom of the complex are presented in Fig. 1.

The results of our investigation on the differentiation of fragmentation patterns in rare earth–acac complexes are in good agreement with relative values of the third ionization potentials of the rare earths already published [12].

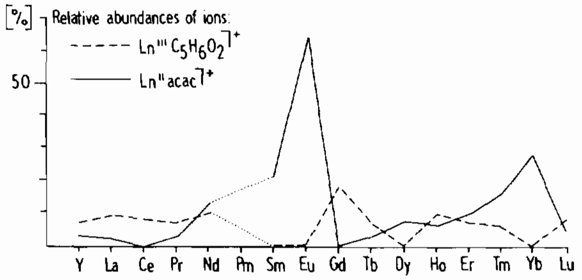


Fig. 1. Relative abundances of the ions $\mathrm{Ln^{III}C_5H_6O_2]^+}$ and $\mathrm{Ln^{II}acac]^+}$ present in electron impact induced fragmentation of Ln(acac)$_3$ complexes.

In conclusion we can ascertain that during mass fragmentation Ce^{III} and Gd^{III} acac complexes always preserve the original oxidation state; complexes with Sm^{III}, Eu^{III} and Yb^{III} undergo a fragmentation with simultaneous change of their oxidation state (III → II), whereas in all the remaining acetylacetonates studied, both types of fragmentation may occur simultaneously.

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