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Mass spectrometric behaviour of M(acac)$_3$ complexes (M = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; acac = acetylacetonate ligand) in triethanolamine upon negative liquid secondary ion mass spectrometry

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Abstract

The series of yttrium and lanthanide (except promethium) acetylacetonates in triethanolamine (TEA) matrix were examined using negative liquid secondary ion mass spectrometry. Deprotonated $[M-H]^-$ molecular ions were observed for all the investigated compounds. Interaction between the complexes studied and the TEA matrix led to formation of polynuclear $[\mathrm{M(TEA\text{-}3H)}]_n$ species, hence the ions produced upon ionization formed adduct-ions with M(acac)$_3$ and $[\mathrm{M(TEA\text{-}3H)}]_n$ neutral particles.

Introduction

β-Diketonate complexes with rare earth cations are well-known in the analytical chemistry of the elements of group 4f [1, 2]. The mass spectrometric behaviour of lanthanide complexes with acetylacetone [3, 4], trifluoroacetylacetone [5], hexafluoroacetylacetone [6], thenoyltrifluoroacetone [7], benzoyltrifluoroacetone [8] or pivaloyltrifluoroacetone [9] upon EI ionization have been previously studied.

In the early 1980s Barber and co-workers developed for mass spectrometry a new method of ionization, fast atom bombardment (FAB), a technique which utilizes a 5–10 keV primary beam of neutral atoms to sputter sample ions from a liquid matrix [10–12]. Presently, extensive application of FAB to organometallic and coordination chemistry is in progress (for reviews see refs. 13, 14).

Application of a liquid matrix is an essential part of FAB-MS or LSI-MS (liquid secondary ion mass spectrometry, a term which includes FAB as well as measurements carried out using accelerated ions as the primary beam [15]. The FAB-MS (LSI-MS) behaviour of a number of compounds has been examined and discussed [16–18]. In our study, we have examined the LSI-MS behaviour of M(acac)$_3$ complexes (M = Y lanthanides, except Pr). For the study triethanolamine (TEA), a widely used, electron-donating matrix was employed and the negative ion mass spectra were recorded.

Behaviour established in the present study also may be applicable to the whole series of the elements of group 4f with various β-diketonate ligands.

Experimental

Mass spectrometric measurements

All negative liquid secondary ion mass spectra were obtained with a two sector MAT 731 instrument combined with a Teknivent Vector/One Workstation. A home-made CsI gun supplied the primary ion beam (6–8 keV, Cs^+). The secondary ion beam was accelerated to 8 kV. Samples were dissolved in dimethyl sulfoxide (DMSO)/acetonitrile (2:1) and the solution was mixed 1:1 with the matrix triethanolamine (TEA). One μl of the mixture was coated onto a stainless steel target (60° angle of incidence, 5.7 mm^2 surface).

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Synthesis of the complexes

The trihydrate yttrium and lanthanide (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) acetylacetonates, $M(acac)_3 \cdot 3H_2O$, were prepared according to the literature [19] and recrystallized from ethanol. Elemental analyses were performed for checking the purity of the complexes: results were in good agreement with the expected formulae (within 0.4%).

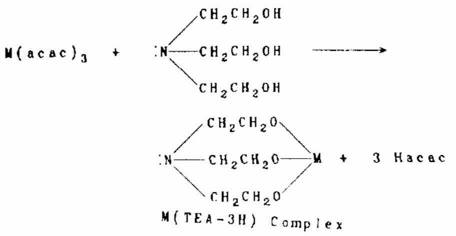
Results and discussion

The negative ion mass spectra of $Y(acac)_3$ and $La(acac)_3$ complexes are shown in Fig. 1. Mass spectral data for the other lanthanides are summarized in Table 1.

In negative liquid secondary ion mass spectrometry of $M(acac)_3$ complexes, a number of pre-ionization, ionization and post-ionization interactions with triethylanolamine have been observed.

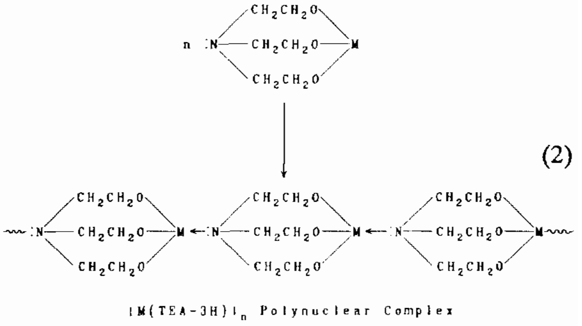
Pre-ionization interactions with TEA

The complexes undergo interaction with triethanolamine to produce the M(TEA-3H) complex.



(1)

Since the metal may accept lone pair electrons, the pair localized on the nitrogen of the TEA moiety may be involved in the formation of a coordination bond. Then, the M(TEA-3H) complex undergoes polymerization to produce polynuclear $[M(TEA\text{-}3H)]_n$ species



(2)

Involvement of an oxygen lone pair to form metal–oxygen coordination bonds, although possible,

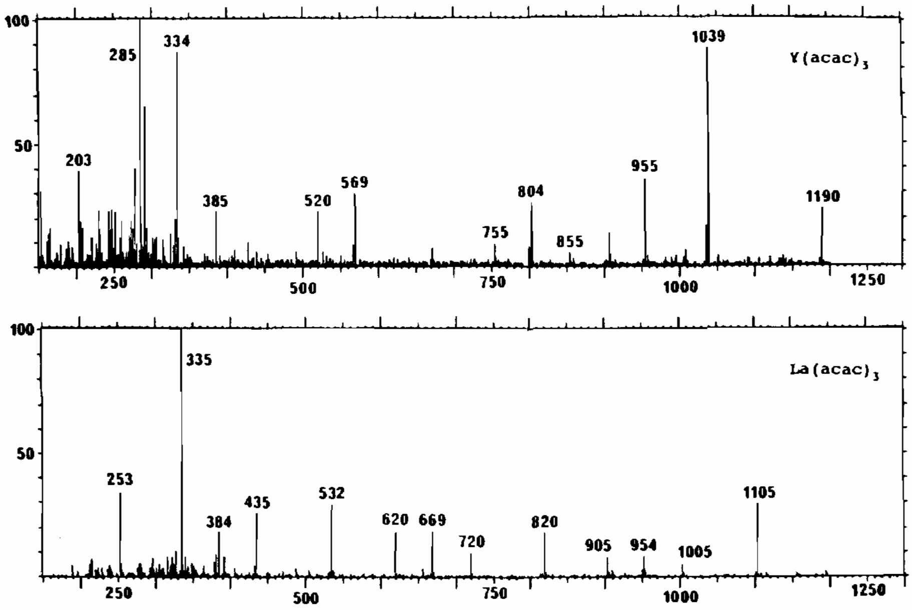


Fig. 1. Negative liquid secondary ion mass spectra of $Y(acac)_3$ and $La(acac)_3$ complexes in 2:1:3 DMSO/acetonitrile/TEA.

TABLE 1. Negative liquid secondary ion data of $Ln(acac)_3$ complexes in 2:1:3 DMSO/acetonitrile/TEA

Elemental composition of the ion	n	Relative intensities (%)													
		Ce[a]	Pr[a]	Nd[b]	Pm[c]	Sm[b]	Eu[b]	Gd[b]	Tb[a]	Dy[b]	Ho[a]	Er[b]	Tm[a]	Yb[b]	Lu[a]
$[M(acac)_2(acac\text{-}H)]^{\bullet -}[M(TEA\text{-}3H)]_n$	0	24	18	20		18	39	27	20	28	21	18	17	13	14
	1	6	8	5		8	13	6	8	12	–	8	3	7	–
	2	8	7	16		6	22	13	6	–	–	8	4	8	8
	3	7	10	8		8	48	–	–	68	–	–	–	–	–
$[M(acac\text{-}H)_2]^{\bullet -}[M(TEA\text{-}3H)]_n$	0	100	100	97		100	30	100	100	100	100	92	100	100	100
	1	15	15	14		15	9	8	15	22	13	16	13	8	19
	2	10	9	10		10	13	10	9	13	11	10	–	10	11
$[O{=}M(acac\text{-}H)]^-$		28	56	47		48	30	42	30	32	26	30	23	10	19
$acac^{\bullet -}[M(TEA\text{-}3H)]_n$	1	95	87	100		99	100	87	82	34	76	100	85	79	81
	2	18	20	18		18	35	23	35	42	26	33	30	17	30
	3	27	28	20		17	30	15	29	28	37	32	29	14	32
	4	43	50	30		29	13	35	30	58	21	45	32	50	35
$acac^{\bullet -}M(acac)_3\cdot[M(TEA\text{-}3H)]_n$	0	30	24	26		14	26	25	16	18	8	6	–	–	–
	1	10	9	8		–	6	6	7	10	–	–	–	–	–
	2	27	27	7		11	–	13	45	12	39	32	31	70	70

[a] Relative intensities of the ions with regard to ^{140}Ce, ^{141}Pr, ^{159}Tb, ^{165}Ho, ^{169}Tm and ^{175}Lu isotopes. [b] Relative intensities of the ions with regard to ^{142}Nd, ^{152}Sm, ^{153}Eu, ^{158}Gd, ^{164}Dy, ^{166}Er and ^{174}Yb isotopes, when the ion contains only one atom of lanthanide. For multi-lanthanide ions is presented the most intense peak of the appropriate cluster. [c] Not investigated.

$$[M(acac)_3]^0 \xrightarrow{-H^+} [M(acac)_2(acac\text{-}H)]^-$$

M	m/z	%
Y	385	23
La	435	27

$$\downarrow -\text{Hacac}$$

$$[M(acac\text{-}H)_2]^-$$

M	m/z	%
Y	285	100
La	335	100

$$\downarrow -CH_3COCH{=}C{=}CH_2$$

$$[O{=}M(acac\text{-}H)]^-$$

M	m/z	%
Y	203	39
La	253	34

Scheme 1. Suggested fragmentation route of $[M-H]^-$ ions.

is less probable. According to previous investigations of Gohlke and McLafferty [20], the electrodonority of the amine group is much higher than that of the hydroxyl group. Therefore, the structure of the polynuclear $[M(TEA\text{-}3H)]_n$ complex, shown in reaction (2), would seem to be correct.

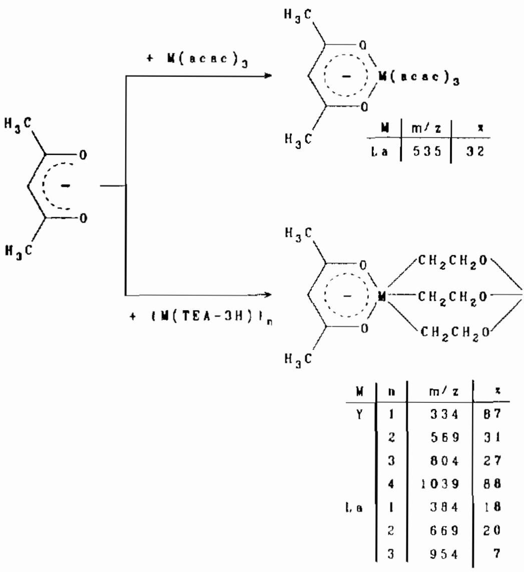
Ionization and post-ionization behaviour of $M(acac)_3$ complexes

The complexes, by substraction of a proton, orm deprotonated even-electron $[M-H]^-$ molecular ions. These may undergo post-ionization decomposition via loss of acetylacetone (Hacac), followed by elimination of $CH_3COCH{=}C{=}CH_2$ neutral species, as shown in Scheme 1.

The above process, similar to decomposition occurring under EI conditions [4], is of great analytical importance, because it provides direct analytical data about the complexes studied. However, since the intensities of ions appearing here may vary or may not be distinguishable in the LSI-MS background, its analytical application may be limited.

Post-ionization processes: formation of adduct ions with $M(acac)_3$ and $[M(TEA\text{-}3H)]_n$ neutral particles

Whereas the M(TEA-3H) complex does undergo proton loss (its $[M-H]^-$ ion is not observed in the recorded mass spectra), the second product of reaction (1), acetylacetone, is observed. Electrodonority of the acac$^-$ ion may be a very effective driving force to produce adduct-ions with the metal-containing neu..al particles:



(3a)

M	m/z	%
La	535	32

(3b)

M	n	m/z	%
Y	1	334	87
	2	569	31
	3	804	27
	4	1039	88
La	1	384	18
	2	669	20
	3	954	7

In the same way, electrodonority of other negative ions formed here (see Scheme 1 and reaction (3a)) have also been involved in the formation of adduct-ions with the $[M(TEA\text{-}3H)]_n$ complex to produce three series of ions.

$$[M(acac)_4]^- \xrightarrow{[M(TEA\text{-}3H)]_n} \{M(acac)_4[M(TEA\text{-}3H)]_n\}^- \quad (4a)$$

M	n	m/z	%
Y	2	955	37
	3	1190	24
La	1	820	17
	2	1105	30

$$[M(acac)_2(acac\text{-}H)]^- \xrightarrow{[M(TEA\text{-}3H)]_n} \{M(acac)_2(acac\text{-}H)[M(TEA\text{-}3H)]_n\}^- \quad (4b)$$

M	n	m/z	%
Y	2	855	6
La	1	720	11
	2	1005	6

$$[M(acac\text{-}H)_2]^- \xrightarrow{[M(TEA\text{-}3H)]_n} \{M(acac\text{-}H)_2[M(TEA\text{-}3H)]_n\}^- \quad (4c)$$

M	n	m/z	%
Y	1	520	28
	2	755	10
La	1	620	18
	2	905	8

The series of ions formed in reactions (3) and (4) are highly characteristic in the recorded spectra (always differing by multiples of the M(TEA-3H) unit. Simultaneously, reactions (3) and (4) are direct confirmation of the previous conclusion, that the desorption process occurring from liquid matrices is not a simple one [21].

Conclusions

By selection of TEA, an effective electron donating matrix, and use of the negative mode of ionization, enhancement of the information content in the LSI-MS mass spectra of $M(acac)_3$ complexes has been observed. Multiplication and shift of important peaks by M(TEA-3H) units make possible their observation in the higher *m/z* region, where the matrix background causes less interference. The spectra suggest that cluster formation occurs in the matrix prior to ionization.

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