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Chemistry of rare earth hypocoordinate oxocluster cations: formation of novel oxoacetate clusters

Alison S. Gajadhar-Plummer [a], Ishenkumba A. Kahwa [a,*], Andrew J.P. White [b], David J. Williams [b]

[a] *Chemistry Department, University of the West Indies, Mona Campus, Kingston 7, Jamaica*
[b] *Chemical Crystallography Laboratory, Chemistry Department, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK*

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Abstract

A fast atom bombardment mass spectrometry (FAB MS) study of $\mathrm{Ln(CH_3COO)_3 \cdot 4H_2O}$ (Ln = Gd (**1**), Y (**2**)) was undertaken to explore the chemistry of hypocoordinate rare earth oxide cations (e.g. $[\mathrm{LnO}]^+$ and $[\mathrm{Ln_3O_4}]^+$), which are frequently encountered in FAB MS of rare earth compounds. A series of novel rare earth oxoacetate clusters, $[\mathrm{Ln}_x\mathrm{O}_x(\mathrm{CH_3COO})_{3x-(2x-1)}]^+$ (**3**) was readily and preferentially obtained over oxide clusters. Oxygenation is important for the stability of large clusters, i.e. **3**, $x \geq 4$. Molecules or molecular ions such as $[\mathrm{LnO}]^+$, $\mathrm{Ln_2O_3}$ and $[\mathrm{Ln_3O_4}]^+$ are coordinatively unsaturated, and may have a more extensive coordination chemistry.

Keywords: FAB mass spectrometry; Rare earth complexes; Oxoacetate complexes; Cluster complexes

1. Introduction

Low ionisation energy mass spectrometry techniques, such as fast atom bombardment mass spectrometry (FAB MS), are good synthetic environments for extremely unusual chemical species. However, there has been limited growth in our understanding of exotic transient chemical species in FAB MS. However, with synthetic techniques advancing to new horizons, as in the case of $\mathrm{C_{60}}$ [1], or more recently $[\mathrm{(CH_3)_3SiOSi(CH_3)_2}]^+$ [2], some of what were fleeting exotic species in mass spectrometers, are now materials with potentially interesting applications!

Difficulties of generating and studying transient species notwithstanding, new information about their physical and chemical behaviour is needed to illuminate our efforts to trap them, or to synthesise their stable derivatives. For example, the most frequently encountered species in the FAB MS of rare earth compounds, are Ln^+ and $[\mathrm{LnO}]^+$ (Ln = La–Lu, Y) [3,4]. The limited data available on the $[\mathrm{LnO}]^+$ molecular ion suggests that $[\mathrm{LnO}]^+$ may have an extensive chemistry [3–5]. For example, the interaction between $[\mathrm{LnO}]^+$ and $\mathrm{(Ln_2O_3)}_n$ produces a series of stable oxoclusters of the general stoichiometry $[\mathrm{Ln}_x\mathrm{O}_{(3x-1)/2}]^+$ [4], the most abundant of which corresponds to $n = 1$, $[\mathrm{Ln_3O_4}]^+$. However, the coordination chemistry (besides condensed oxides) of the hypocoordinate monomeric $[\mathrm{LnO}]^+$ species, is either unknown, or is very poorly defined [5]. This dearth of chemical knowledge, is detrimental to efforts to understand the origin and stabilisation of such species, as well as to the exploration of their scientific and technological potential.

We have explored the coordination chemistry of $[\mathrm{LnO}]^+$ species using the acetate anion, which is known to form crystalline mono-oxide clusters, such as $[\mathrm{Zn_4O(CH_3COO)_6}]$ [6] and $[\mathrm{Mn_3O(CH_3COO)_6(3Cl\text{-}pyr)_3}]$ [7]. Whereas great care is needed in using solid state observations to infer chemical behaviour in special environments such as FAB MS, the remarkable ability of the acetate chelate to adjust to a variety of coordination requirements of $\mathrm{Ln^{3+}}$ ions [8–11], makes it a particularly encouraging choice for our $[\mathrm{LnO}]^+$ coordination studies. It was necessary to use well-defined starting materials for our FAB MS studies, since a previous study employing commercial rare earth acetates, produced interesting species, albeit, having strange isotopic abundance patterns and Ln oxidation states [12]. We chose the crystalline $\mathrm{Gd(CH_3COO)_3 \cdot 4H_2O}$ (**1**) as a starting material in our FAB MS studies, in order to take advantage of the

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* Corresponding author. Tel.: +1-809-927-1910; fax: +1-809-977-1835; e-mail: ikahwa@uwimona.edu.jm

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polyisotopic nature of gadolinium in making m/z assignments, and the coordinated water in the $[\{(H_2O)_2(CH_3COO)_2Gd\text{–}(\mu\text{-}CH_3COO)_2\text{–}Gd(CH_3COO)_2(H_2O)_2\}\cdot 4H_2O]_n$ dimeric repeating unit [8], to generate oxoclusters with minimum damage to the acetate chelates. Further, we studied the yttrium analogue $Y(CH_3COO_3)\cdot 3H_2O$ (**2**) in the hope of generating and detecting larger clusters, because of the smaller mass number of this mono-isotopic rare earth element.

Herein we report the formation of novel rare earth oxoacetate clusters of the general stoichiometry $[(Ln_xO_y)(CH_3COO)_{3x-(2y+1)}]^+$ (**3**).

2. Experimental

2.1. Materials

Lanthanide nitrates were obtained by neutralising the corresponding oxides (Aldrich, 99.99% purity) with nitric acid. Acetic acid (50%) was from BDH.

2.2. Synthesis

Compounds **1** and **2** were synthesised by boiling $Ln(NO_3)_3\cdot nH_2O$ in 50% acetic acid; the product obtained was recrystallised from water to give white transparent crystals.

2.3. Analysis

The identity of **1** was established conclusively using single-crystal X-ray diffraction analysis; the structure is isomorphous with that reported by Favas et al. [8]. *Anal.* **1**, $GdC_6H_{17}O_{10}$. Found: C, 17.95; H, 3.90. Calc.: C, 17.7; H, 4.2%. **2**, $YC_6H_{15}O_9$. Found: C, 22.62; H, 4.73. Calc.: C, 22.5; H, 4.7%.

The FAB MS spectra were acquired with samples in a *m*-nitrobenzoyl alcohol (*m*-NBA) matrix, using an AutoSpecQ mass spectrometer.

The computer programme used to deconvolute the isotopic patterns was Isopro V 2.1, written by J.A. Yergey from Sheffield University, UK [1].

3. Results

Bombardment of **1** and **2** with fast Xe atoms under the mild ionising conditions of FAB MS, leads to the formation of a variety of novel yttrium and gadolinium oxoacetate clusters (Figs. 1 and 2, Table 1). Except for a few hydrated (b, e, j, and r) and hydroxy (f, g, and k) complex cations, the oxoacetate clusters formed are predominantly anhydrous species of lanthanide(III) ions, and conform to the general formula, $[(Ln_xO_y)(CH_3COO)_{3x-(2y+1)}]^+$ (**3**). For the FAB MS spectra of **1**, observed isotopic abundance patterns (Fig. 1(a)) of the clusters, generally match satisfactorily with the simulated ones (Fig. 1(b)). Larger clusters were better defined when the matrix was wet, i.e. during the initial moments of the FAB MS experiment (Fig. 1, clusters o–d′).

Table 1
Principal gaseous species found in the FAB MS of **1** and **2** [a]

Symbol	Cluster	Ln^{3+} = Gd		Ln^{3+} = Y	
			I (%)		*I* (%) (×3)
a	$[LnL_2]^+$	✓	30	–	–
b	$[LnL_3(H_3O)]^+$	✓	44	✓	18
c	$[Ln_2O_2L]^+$	✓	34	✓	80
d	$[Ln_2O_3L]^+$	✓	75	✓	96
e	$[Ln_2OL_3(H_2O)]^+$	–	–	✓	35
f	$[Ln_2L_4(OH)]^+$	✓	22	–	–
g	$[Ln_2L_4(OH)(H_2O)]^+$	–	–	✓	38
h	$[Ln_2L_5]^+$	✓	95	✓	75
i	$[Ln_3O_3L_2]^+$	✓	20	✓	37
j	$[Ln_2L_6(H_3O)]^+$	✓	38	✓	44
k	$[Ln_3O_2L_3(OH)]^+$	✓	30	✓	57
l	$[Ln_3O_2L_4]^+$	✓	18	✓	20
m	$[Ln_3OL_6]^+$	✓	90	✓	83
n	$[Ln_4O_4L_3]^+$	✓	17	✓	57
o	$[Ln_3L_8]^+$	✓	45	✓	14
p	$[Ln_4O_3L_5]^+$	✓	78	✓	22
q	$[Ln_5O_6L_2]^+$	✓	33	✓	46
r	$[Ln_3L_9(H_3O)]^+$	x	15	✓	16
s	$[Ln_4O_2L_7]^+$	✓	66	✓	32
t	$[Ln_5O_5L_4]^+$	✓	66	✓	40
u	$[Ln_4OL_9]^+$	✓	94	✓	65
v	$[Ln_5O_4L_6]^+$	✓	33	✓	20
w	$[Ln_4L_{11}]^+$	x	20	✓	17
x	$[Ln_5O_3L_8]^+$	x	12	✓	4
y	$[Ln_6O_6L_5]^+$	✓	32	✓	4
z	$[Ln_5O_2L_{10}]^+$	✓	66	✓	7
a′	$[Ln_6O_5L_7]^+$	x	22	✓	24
b′	$[Ln_5OL_{12}]^+$	x	16	✓	4
c′	$[Ln_6O_3L_{11}]^+$	✓	26	✓	5
d′	$[Ln_6O_2L_{13}]^+$	✓	30	✓	12

[a] L = CH_3COO^-; *I* = intensity; ✓ = observed and calculated isotopic intensity pattern matched well; x = observed and calculated isotopic intensity pattern matched unsatisfactorily; – = no peak was observed for the species.

The most important result of this experiment, however, is the dramatic effect of oxygen content on the intensities of oxoacetate clusters **3**. The preponderance of the evidence shows that oxygenation of the lanthanide acetates increases the yield of large clusters (Figs. 3 and 4); however, the roughly sinusoidal relationship between cluster intensity and oxygen content, is a complication which suggests that other factors are important. Generally, the most abundant species when $x > 4$, are the oxygen-rich penta- and hexa-oxoacetates (q, t, y, a′); large non-oxygenated acetate clusters of **3** with $x = 5$, 6 and $y = 0$, are not observed (Figs. 1 and 2). The unusually high abundance of the gadolinium dioxoacetate, z, compared with its yttrium counterpart (Table 1) is excep-

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[1] Available on the Internet at the web site: http://www.chem.schef.ac.uk./webelements.cgi$isot

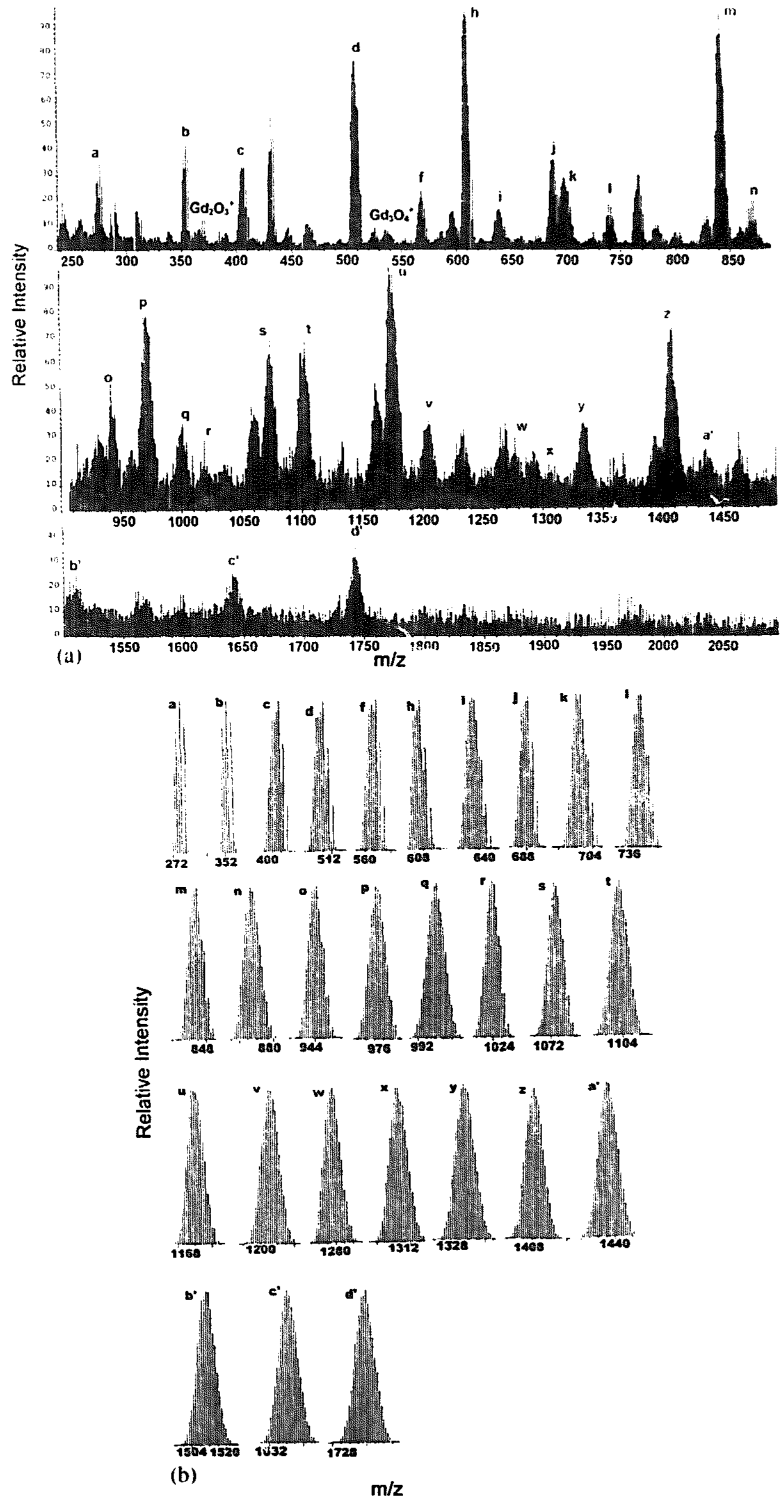

Fig. 1. (a) Isotopic abundance patterns for a series of species formed by the fast atom bombardment of $[Gd(CH_3COO)_3(H_2O)_2]_2 \cdot 4H_2O$ in a *m*-NBA. (b) Simulated isotopic abundances for gadolinium species.

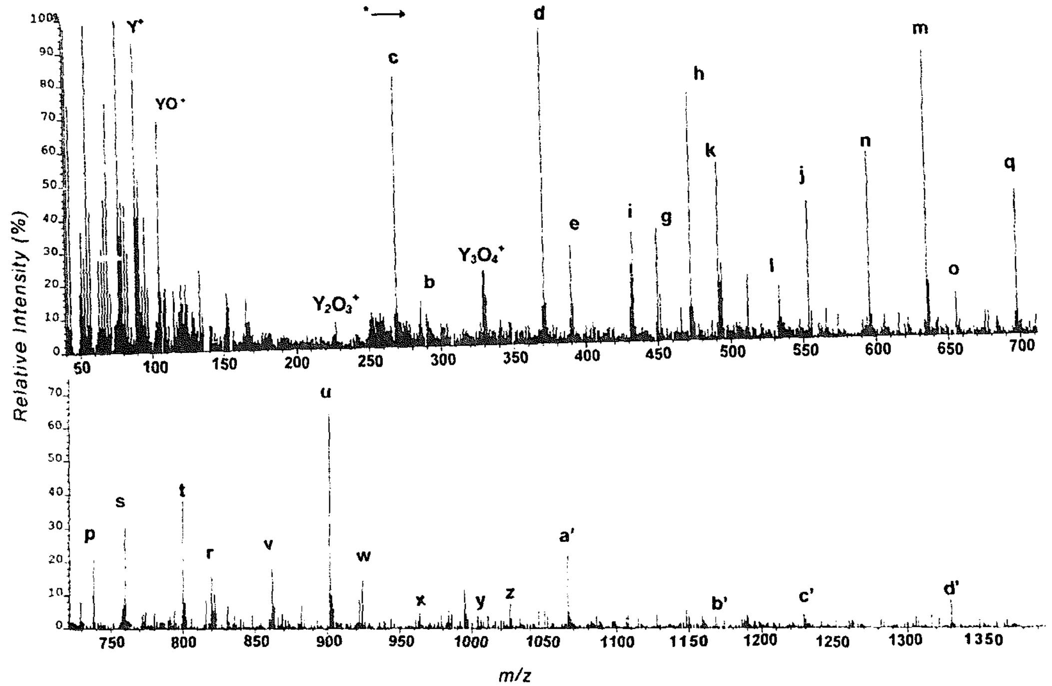

Fig. 2. The FAB MS spectrum of $[Y(CH_3COO)_3(H_2O)_2]_2\cdot 3H_2O$ in a m-NBA matrix; sensitivities after *→, ×3.

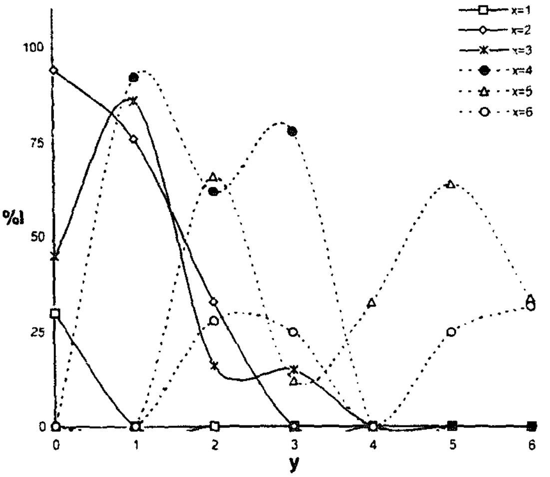

Fig. 3. Plot of oxoacetate cluster intensities against oxygen content, y, for $[Gd_xO_y(CH_3COO)_{(3x-2y-1)}]^+$: ——— experiment done under dry conditions; ······ experiment done under wet matrix conditions.

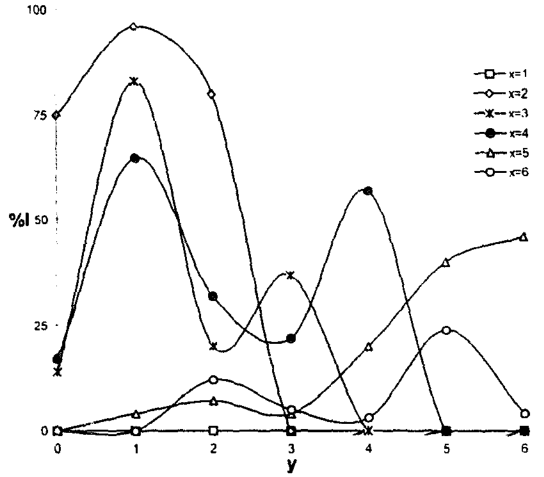

Fig. 4. Plot of oxoacetate cluster intensities against oxygen content, y, for $[Y_xO_y(CH_3COO)_{(3x-2y-1)}]^+$.

tional, and we have no explanation for it. Similar unusual behaviour is exhibited by gadolinium di- and tri-oxoacetates, s and p, respectively. For $x \leq 4$, all oxoacetate clusters of yttrium(III) are more abundant than the corresponding non-oxygenated acetates (Figs. 2 and 4). This is also true for gadolinium(III) species, when $x=4$ and 3 ($y=1$); however, for $x=2$, the pure acetate species (h) is the most abundant.

A few pure oxoclusters were obtained in very low abundances in the FAB MS of **1** and **2** (Figs. 1(a) and 2). The preference for the formation of clusters with an odd number of rare earth atoms, which was a dominant feature in the FAB MS results involving binary oxoclusters [3,5], was not observed for the oxoacetate clusters.

Overall, the acetate of the larger gadolinium(III) ion is a better source of high oxoacetate cluster intensities than the acetate of the smaller rare earth ion, yttrium(III).

4. Discussion

The high abundances of the pure acetates, $[Ln_2(CH_3COO)_5]^+$, and the mono-oxoacetates, $[Ln_2O(CH_3COO)_3]^+$, along with the low intensities of the hydrated and hydroxy species, are consistent with extensive chemical modifications of the supramolecular array of **1** and **2** in the FAB MS environment. Given the crystal structures of **1** [8] and **2** [13], the dominance of the $[Ln_2(CH_3COO)_5]^+$ species is not surprising, since the dimeric molecule $[(H_2O)_2(CH_3COO)_2Gd–(\mu\text{-}CH_3COO)_2–Gd(CH_3COO)_2(H_2O)_2]$, is the repeating unit of the supramolecular motif held together by hydrogen bonding.

It is, however, strange that the hydrophilic Ln^{3+} ions lost their coordinated water, thereby enabling anhydrous species such as $[Ln(CH_3COO)_2]^+$, $Ln(CH_3COO)_3$, and $[Ln_2(CH_3COO)_5]^+$ with coordinatively unsaturated Ln^{3+} sites to be stabilised. Generally, coordinated water such as that of **1** and **2** is very difficult to remove; thermogravimetric studies show that dehydration of coordinated water in $[(H_2O)_2(CH_3COO)_2Gd–(\mu\text{-}CH_3COO)_2–Gd(CH_3COO)_2(H_2O)_2]$ requires heating to 200–220°C [14]. However, entropic and enthalpic factors associated with extended H-bonding interactions between coordinated water and the polar protic *m*-NBA matrix, may encourage dehydration of the Ln^{3+} sites.

The formation of the oxoclusters is evident in the FAB mass spectra of both **1** and **2**, $[YO]^+$ being the most intense species for **2** (Fig. 2). Of the oxoacetates formed by **1** and **2**, the mono-oxoacetates $[Ln_2O(CH_3COO)_3]^+$ and $[Ln_3O(CH_3COO)_6]^+$, are the most abundant (Table 1). We therefore propose that these mono-oxoacetates are generated by the condensation reaction of the very abundant monomeric oxide $[LnO]^+$, with monomeric and dimeric acetates $Ln(CH_3COO)_3$ and $Ln_2(CH_3COO)_6$. Such reactions are favourable in the 'soup of sputtered particulates', just above the matrix, where reactant concentrations are reasonable [4]. Thus, cluster formation can, in this scheme, occur via a series of condensation reactions involving the lanthanide oxides, $[Ln_xO_{(3x-1)/2}]^+$ and the anhydrous acetates, as shown in Eqs. (1)–(7):

$$(m\text{-NBA}) + Ln(CH_3COO)_3 \cdot 4H_2O \xrightarrow{\text{fast Xe atoms}} Ln^+ + [Ln_xO_{(3x-1)/2}]^+ + [Ln_x(CH_3COO)_{(3x-1)}]^+ + Ln_x(CH_3COO)_{3x} + H_2O + CH_3COO^- \ldots \quad (1)$$

For the mono-oxoacetates, d, m, u, and b′:

$$[LnO]^+ + [Ln_x(CH_3COO)_{3x}] \rightarrow [Ln_{x+1}O(CH_3COO)_{3x}]^+ \quad (2)$$

Since the intensities of the anhydrous acetates, $[Ln_x(CH_3COO)_{3x-1}]^+$ (h, o, w), show a decreasing trend with increasing x, it is reasonable to expect that this would also be the case for the neutral $Ln_x(CH_3COO)_{3x}$ species.

Correspondingly, the abundances of the mono-oxoacetates, $[Ln_{x+1}O(CH_3COO)_{3x}]^+$, also exhibit a decreasing trend with increasing x.

For the di-oxoacetates (c, l, s, z, d′) (Table 1, Figs. 1(a) and 2), the reduced species $[Ln_2O_2]^+$ (or two $[LnO]^+$) are the likely sources of the two oxygens. A three- or four- body process is, however necessary to yield the di-oxoacetates:

$$[Ln_2O_2]^+ + [Ln_x(CH_3COO)_{3x}] + CH_3COO^- \rightarrow [Ln_{x+2}O_2(CH_3COO)_{3x+1}]^+ \quad (3a)$$

$$[LnO]^+ + [LnO]^+ + [Ln_x(CH_3COO)_{3x}] + (CH_3COO)^- \rightarrow [Ln_{x+2}O_2(CH_3COO)_{3x+1}]^+ \quad (3b)$$

Reactions between three or four species are less likely to occur than those requiring just two. This may explain the sharp drop in intensities of $[Ln_xO_y(CH_3COO)_{3x-(2y+1)}]^+$ at $y=2$, which is most evident for $x<4$. The tri-, tetra-, penta-, and hexa-oxoacetates can be generated in processes similar to those of Eqs. (2) and (3) using Ln_2O_3, $[Ln_3O_4]^+$, $[Ln_4O_5]^+$, and Ln_4O_6, as proposed in Eqs. (4)–(7):

$$Ln_2O_3 + [Ln_x(CH_3COO)_{3x-1}]^+ \rightarrow [Ln_{x+2}O_3(CH_3COO)_{3x-1}]^+ \quad (4)$$

$$[Ln_3O_4]^+ + [Ln_x(CH_3COO)_{3x}] \rightarrow [Ln_{x+3}O_4(CH_3COO)_{3x}]^+ \quad (5)$$

$$[Ln_4O_5]^+ + Ln_x(CH_3COO)_{3x} + (CH_3COO \rightarrow [Ln_{x+4}O_5(CH_3COO)_{3x+1}]^+ \quad (6)$$

$$[Ln_4O_6 + [Ln_x(CH_3COO)_{3x-1}]^+ \rightarrow [Ln_{x+4}O_6(CH_3COO)_{3x-1}]^+ \quad (7)$$

The comparatively low abundances of the di-, tri-, tetra-, penta-, and hexa-oxoacetates (Table 1) may be rationalised on the basis of the inefficiencies of reactions (4)–(7), due in part to the low reactant concentrations in the 'sputtered soup' [4]. However, the apparent stabilising influence of oxygenation on large clusters (Figs. 3 and 4) is remarkable. With stoichiometries $[Ln_xO_y(CH_3COO)_{3x-(2y+1)}]^+$ having $x>4$, non-oxygenated species are not observed; while for $x=6$, even the mono-oxoacetate is unobservable. Clearly, greater oxygenation corresponds to favourable formation of large clusters (Figs. 3 and 4). We suggest that this is due to thermodynamic effects, rather than oxoacetate cluster formation kinetics; the strongly oxophilic nature of Ln^{3+} ions contributes significantly to the stability of the larger oxoacetate clusters. This conclusion is justified in view of the observations made during earlier collision induced dissociation [4] studies of oxoclusters, in which the very abundant $[Ln_xO_{(3x-1)/2}]^+$ ions were also found to be very stable, while the less abundant $[Ln_xO_{3x/2}]^+$ oxides were extremely unstable.

Finally, we compare the FAB MS properties of **1** and **2**. While the compounds used in the FAB MS studies were carefully chosen to optimise similarities in Ln^{3+} radii, hence chemical behaviour, subtle manifestation of the lanthanide contraction is evident (Figs. 3 and 4). The anticipated higher abundances of large yttrium oxoacetates did not materialise, and generally, judging from cluster intensities, the larger gadolinium(III) ion ($r_+ = 0.938$ Å) [15] seems to be a better oxoacetate former than the smaller yttrium(III) ion ($r_+ = 0.892$ Å) [15] (Table 1). This contrast is in spite of the relatively higher preference for yttrium(III) oxoacetate clusters, compared with pure acetates; for example, the intensity of the mono-oxoacetate, d, is higher than that of the corresponding pure acetate, h (Table 1). By contrast, for gadolinium, the intensity of h is noticeably higher than that of d. We propose that gadolinium(III) forms more stable large oxoacetate clusters than does yttrium(III). Although both Gd^{3+} and Y^{3+} can bind to the acetate anion in a variety of ways [8–11], ranging from bidentate, to bidentate-bridging and monodentate-bridging, the cationic radii differential may be important when the incoming oxygen bridges several Ln^{3+} ions. This may strain the sp^2 carboxylate ligand bite, thereby reducing the cluster stability because of poor Ln^{3+} acetate interactions. This is not important for the dilanthanide species $[Ln_2O(CH_3COO)_3]^+$, where there are no competing Ln–O–Ln linkages; thus the oxoacetate $[Y_2O(CH_3COO)_3]^+$ (d) is even more abundant than the acetate dimer $[Y_2(CH_3COO)_5]^+$ (h) (Table 1).

In conclusion, this FAB MS study reveals preferential formation of rare earth oxoacetates over that of the pure oxides, oxygenated polymetallic clusters being more favourable, especially for the larger Gd^{3+} ions. The condensations leading to polymetallic oxides studied in detail earlier [4], and the discovery of the above oxoacetates demonstrate that oxoclusters such as $[LnO]^+$, $[Ln_2O_2]^+$, $[Ln_2O_3]^+$ and $[Ln_3O_4]^+$ found in the FAB MS, are truly hypocoordinated. There may be an interesting and more extensive coordination chemistry for simple oxides such as $[LnO]^+$, which could be relevant to the search for rare earth compounds and materials exhibiting novel physical and chemical properties. In this regard, recent claims of the syntheses of polymeric compounds containing clusters such as $[(DMF)_{16}Yb_6(OH)_8(\mu_6\text{-}O)]^{8+}$ [16], $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{12}(NO_3)_6](NO_3)_2 \cdot xH_2O$ [17], and $[Eu_8(DMF)_{13}(\mu_4\text{-}O)(\mu_4\text{-}OH)_{12}(Se_3)(Se_4)_2(Se_5)_2]$ [18] are encouraging.

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