Electrospray mass spectrometry of lanthanide β-diketone complexes Part 1. Ligand exchange processes involving acetate ions and $Ln(thd)_3$ complexes (Ln = Eu, Gd, Yb; thd = 2,2,6,6-tetramethyl-3,5-heptanedione)

Jonathan M. Curtis, Peter J. Derrick
Warwick Institute of Mass Spectrometry and Department of Chemistry, University of Warwick, Coventry (UK)

André Schnell, Emily Constantin
Université Louis Pasteur, Strasbourg (France)

Richard T. Gallagher and John R. Chapman
Kratos Analytical, Barton Dock Road, Urmston, Manchester (UK)

(Received April 10, 1992; revised June 4, 1992)

Abstract

The electrospray mass spectra of the lanthanide (Ln) 2,2,6,6-tetramethyl-3,5-heptanedione (thd) complexes $Eu(thd)_3$, $Gd(thd)_3$ and $Yb(thd)_3$ were obtained from a methanol/water solution containing acetic acid. Protonated molecular ions $Ln(thd)_3H^+$ were obtained in each case. Extensive ligand exchange reactions in solution resulted in many mixed-ligand cationic species involving acetato ligands, H_2O and H^+. Tandem mass spectrometry of $Ln(thd)_3H^+$ gave the fragment ions $Ln(thd)^+$ containing a lanthanide in the divalent state for Eu and Yb.

Introduction

Negative liquid secondary ion mass spectrometry (LSIMS) was recently applied to some β-diketonate complexes of rare earth cations [1]. In that study lanthanide acetylacetone (acac) complexes in a liquid matrix of triethanolamine (TEA) were ionized by bombardment with 8 keV Cs^+ ions. The complexes readily form deprotonated even electron $[M-H]^-$ molecular ions which could undergo post-ionization decomposition to yield $[Ln(acac-H)_2]^-$ and $[O{=}Ln(acac-H)]^-$ in high abundance. In addition the formation of adduct ions was observed and explained in terms of reactions with [Ln(TEA-3H)]*n* neutral species and involving $acac^-$ anions. The resulting ligand exchange produces an abundance of information on the formation and stability of such ionic complexes although it is difficult to determine the mechanisms of their formation since reactions may occur pre- or post-ionization.

An alternative approach was adopted here for the ionization of β-diketone complexes of some lanthanides and for the study of ligand-exchange processes, by the use of electrospray ionization (ES). ES ionization is a newly developed method suitable for the analysis of polar and labile compounds in a range of relative molecular masses (RMMs) extending to beyond 10^5 [2–5]. For this reason, it has been widely applied to the analysis of large biomolecules [2]. Electrospray mass spectrometry (ESMS) has been described [2] as taking place in three consecutive steps. The first step is the production of small, highly charged droplets which are produced by spraying the analyte in solution from a needle held at high voltage. The second step is desorption of analyte ions from the droplet surface in an atmospheric pressure ion source. Finally the analyte ions are sampled for analysis into the vacuum system of a mass spectrometer. Although there is some debate over the exact mechanism of ion formation by ES ionization, it does appear that ions are preformed in the droplet, i.e. in the liquid phase. The initial developments of ESMS took place using quadrupole mass analysers, as a result of their lower ion-source voltages and pumping requirements coupled with an adequate range of mass-to-charge (*m/z*) ratios to detect often highly charged molecular species. More recently, ESMS using double focusing sector mass spectrometer, which offers both a higher mass resolution and a larger *m/z* range, has been described [6]. In this study, we have used electrospray ionization in combination with a four-sector mass spectrometer — essentially two double-fo-

0020-1693/92/$5.00

cusing mass spectrometers (MS1 and MS2) in tandem. In this way, an ionic species can be selected by MS1 and following collision with a rare gas target atom, its fragment-ion spectrum can be recorded by an appropriate scan of MS2. Hence structural information on the selected 'parent' ion can be obtained.

Experimental

Mass spectrometry

All spectra were obtained using a Kratos Concept IIHH four-sector mass spectrometer and processed using the Kratos Mach 3 software (Kratos Analytical, Manchester, UK). A standard Kratos electrospray ion source was used which is based on the published design [6]. Briefly, the analyte solution is sprayed from the tip of a needle at about 8 kV towards the first skimmer at about 5kV, through a countercurrent flow of nitrogen gas. Between the first and second skimmer is a region pumped by a rotary pump to a pressure of around 20 torr. The second skimmer defines the energy of ions entering the mass spectrometer, which was set to transmit ions having 4 keV of translational energy. Between the second and third skimmers is a region pumped by a turbomolecular pump down to a typical pressure of 10^{-5} torr. Beyond the third skimmer at a pressure of $<10^{-6}$ torr lie some transfer optics to focus the ion beam onto the entrance slit to the mass spectrometer (i.e. the source slit). The electrospray source was heated to around 70 °C. FAB mass spectra utilized an Ion Tech saddle field ion gun producing a beam of Xe atoms at 8 keV, and a standard Kratos FAB source with an accelerating voltage of 8kV.

All mass spectra were recorded as raw data at scan speeds of 10 s/decade over the mass range 1500–100. Tandem mass spectra (MS/MS spectra) used a scan speed of 30 s per decade with the collision cell at 2 kV (i.e. a collision energy of 2 keV). The DS90 data system was used to calculate the B/E linked scan of MS2 appropriate to the parent ion mass within the calibrated mass range of 1800–14 for 4 keV ions. Helium was the collision gas used in all experiments.

Sample preparation

All samples were dissolved in a 1:1 solution of MeOH/H_2O containing 1% acetic acid. Liquid flow to the needle used a Harvard 22 Syringe Pump (Harvard Apparatus Inc., South Natick, MA, USA) producing flow rates in the 1–10 μl min^{-1} range. Samples were added to the solvent flow via a 20 μl Rheodyne injector valve (model 7120). The lanthanide complexes $Ln(thd)_3$, where Ln = Eu, Gd or Yb, were obtained from MTM Research Chemicals Ltd., Morecambe, Lancashire, UK, and were used as received.

Results and discussion

The electrospray mass spectra of $Ln(thd)_3$, where thd is 2,2,6,6-tetramethyl-3,5-heptanedione; Ln = Eu, Gd, Yb, were obtained using a mobile phase of 1:1 MeOH/H_2O with 1% acetic acid. The general features of the electrospray mass spectra of $Eu(thd)_3$, $Gd(thd)_3$ and $Yb(thd)_3$ are remarkably similar under the present experimental conditions, as summarized in Table 1. The relative intensities given in Table 1 are the results for a set of experiments performed under nominally identical conditions, but were found to show substantial day-to-day variations. This is probably due to varying spray conditions and difficulties in solubilizing the rare-earth compounds. However, such irreproducibilities did not alter the ions actually present in the spectra. Thus Table 1 gives a reliable guide to the ions observed, but the relative intensities given do not show the kind of reproducibility expected from, for example, electron impact mass spectra [7], but are akin to other ionization methods involving liquid–vacuum interfaces e.g. thermospray [8] or FAB [9].

The ES mass spectrum of $Eu(thd)_3$ is shown in Fig. 1. The base peak in the spectrum corresponds to protonation of the intact molecule, i.e. $Eu(thd)_3H^+$. In addition, the spectrum contains intense peaks (see Table 1) corresponding to the loss of [thd + H] forming $Eu^{III}(thd)_2{}^+$ and a further loss of thd ligand accompanied by a reduction of the Eu from the predominant +3 oxidation state to the +2 oxidation state to give $Eu^{II}(thd)^+$. Analogous changes in oxidation state have been reported previously in the electron impact mass spectra of lanthanide complexes [10, 11].

TABLE 1. The relative intensities of the major species in the electrospray mass spectra of $Ln(thd)_3$ complexes in 1:1 MeOH/H_2O with 1% acetic acid

Assigned formula	Relative intensity (%)		
	Eu	Gd[a]	Yb
$Ln_2(thd)_3(AcO)_2{}^+$	4		2
$Ln_2(thd)_2(AcO)_3{}^+$	17	13 (20)	10
$Ln_2(thd)(AcO)_4{}^+$	21	19 (30)	8
$Ln(thd)_3H^+$	100	64 (100)	100
$Ln(thd)_2(AcO)(H_2O)H^+$	61	73 (114)	60
$Ln(thd)_2(AcO)H^+$	22	31 (48)	20
$Ln(thd)_2{}^+$	37	100 (156)	72
$Ln(thd)(AcO)_2(H_2O)H^+$	34	68 (106)	25
$Ln(thd)(AcO)_2H^+$	5	11 (17)	12
$Ln(thd)(AcO)^+$	21	83 (130)	11
$Ln(thd)^+$	28		
$Ln(AcO)_3(H_2O)H^+$		12 (25)	
$Ln(AcO)_2{}^+$		16 (19)	
$[Ln(thd)_3 + 2H]^{2+}$	3		15

[a]Figures in parentheses are normalised to value for $Gd(thd)_3H^+$.

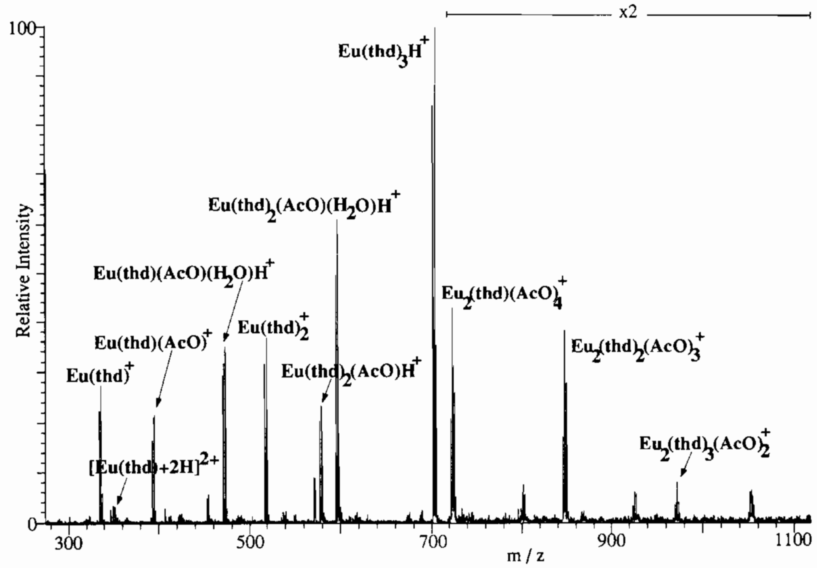

Fig. 1. The electrospray mass spectrum of $Eu(thd)_3$ in $MeOH/H_2O$ with 1% acetic acid.

The remainder of the peaks in the spectrum can be accounted for in terms of ligand exchange and clustering reactions. Ligand exchange involving acetato ligands $(AcO)^-$ results in the four coordinate $[Eu(thd)(AcO)]^+$. Successive exchanges of thd by AcO^- ligands results in the series of ions containing two europium atoms $[Eu_2(thd)_3(AcO)_2]^+$, $[Eu_2(thd)_2(AcO)_3]^+$ and $[Eu_2(thd)(AcO)_4]^+$ in order of increasing intensity and degree of substitution. Also present in high abundance are ions at 78 mass units higher than both $[Eu(thd)_2]^+$ and $[Eu(thd)(AcO)]^+$. These ions may be the protonated neutral complexes $[Eu(thd)_2(AcO)(H_2O)]H^+$ and $[Eu(thd)(AcO)_2(H_2O)]H^+$ where the proton is associated with an oxygen either on a thd ligand, as with the case of $[Eu(thd)_3]H^+$ or on an acetato ligand. Consistent with this suggestion are the ions at 18 units lower, assumed to be $[Eu(thd)_2(AcO)]H^+$ and $[Eu(thd)(AcO)_2]H^+$, respectively, although these are present in much lower intensity than their monohydrated counterparts. However, an alternative interpretation is that, for example the ion at *m/z* 597 could be described as $[Eu(thd)_2(AcOH)(H_2O)]^+$ rather than $[Eu(thd)(AcO)(H_2O)]H^+$. The dication $[Eu(thd)_3+2H]^{2+}$ is present at about 5% abundance, but it should be noted that ions seen at twice the *m/z* where the corresponding monocations would be observed (i.e. at 704.7 for ^{153}Eu) are solely due to the ^{13}C isotopes of $[Eu(thd)_3]H^+$. The presence of $[Eu(thd)_3+2H]^{2+}$ is confirmed by the separation of the isotope peaks being exactly half that for a monocation.

The electrospray mass spectrum of $Gd(thd)_3$ (see Fig. 2) differs from that of $Eu(thd)_3$ and $Yb(thd)_3$ in several ways. First there is greater abundance of ions arising from substitution or loss of one or two thd ligands, the two most intense peaks being $Gd(thd)_2{}^+$ (the base peak) and $Gd(thd)(AcO)^+$. These are both four-coordinate species, the six-coordinate species being of slightly lower abundance. Another difference is the presence of the two additional ions $Gd(AcO)_3(H_2O)H^+$ and $Gd(AcO)_2{}^+$, neither of which are present for Eu or Yb.

The electrospray mass spectrum of $Eu(thd)_3$ is distinct in that it is the only one exhibiting the +2 oxidation state of the rare earth element. The stability of complexes of the +2 oxidation state is also illustrated by the MS/MS spectra of the three $Ln(thd)_3H^+$ complexes, as shown in Fig. 3, and in Table 2. These were obtained by selecting a monoisotopic species in MS1 (e.g. $^{153}Eu(thd)_3H^+$), attenuating the ion beam by 70% by collisions with helium atoms in the intermediate gas cell, and recording a fragment ion spectrum by scanning MS2. Figure 3(a) shows the helium collision-induced dissociation (CID) spectrum of $^{153}Eu(thd)_3H^+$ ions formed by electrospray ionization. In addition to the precursor ion $Eu(thd)_3H^+$, the CID spectrum is dominated by only two fragment ions – the loss of (thd + H) to give $Eu(thd)_2{}^+$, and the loss of (2thd + H) to give $Eu(thd)^+$. Notice that the latter ion represents a change in oxidation state from +3 to +2 following collisional activation, which occurs in high abundance (see Table 2). In contrast, $^{158}Gd(thd)_3H^+$ fragments to give $Gd(thd)_2{}^+$ only (Fig. 3(b)), whilst $^{174}Yb(thd)_3H^+$ gives $Yb(thd)_2{}^+$ most abundantly, and $Yb(thd)^+$ weakly (Fig. 3(c) and Table 2).

The three spectra shown in Fig. 3 were all recorded during the same session using the same conditions, so should allow a reliable comparison to be made. The abundance of the $Ln^{II}(thd)^+$ species in the CID spectra is in the order $Eu > Yb \gg Gd$ (55:8:0 relative to the unattenuated precursor ion). It is well known in lan-

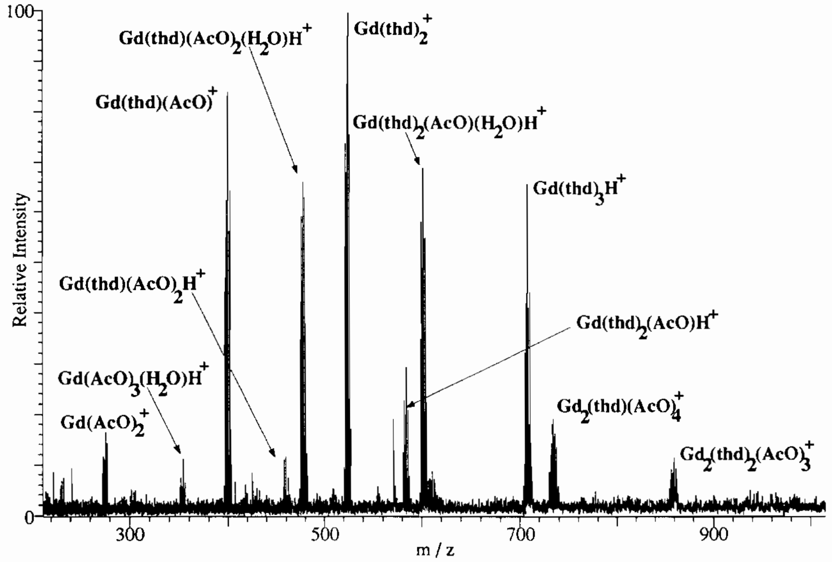

Fig. 2. The electrospray mass spectrum of Gd(thd)$_3$ in MeOH/H$_2$O with 1% acetic acid.

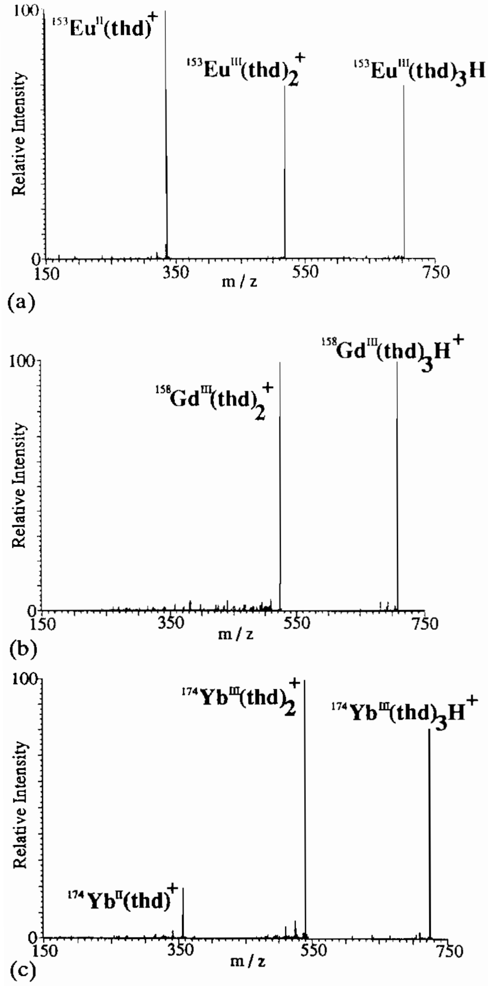

Fig. 3. MS/MS spectra of Ln(thd)$_3$H$^+$ ions formed by electrospray ionization, using He CID with a beam attenuation of 70% and a collision energy of 2keV. (a) ^{153}Eu(thd)$_3$H$^+$; (b) ^{158}Gd(thd)$_3$H$^+$; (c) ^{174}Yb(thd)$_3$H$^+$.

TABLE 2. The relative intensities of the major peaks in the He CID spectra of Ln(thd)H$^+$ ions for Ln = ^{153}Eu, ^{158}Gd and ^{174}Yb. A beam attenuation of 70% was used, and the collision energy was 2 keV. Figures are relative to 100% for the attenuated precursor ion

Species	Ln		
	Eu	Gd	Yb
^{a}Ln(thd)$_3$H$^+$	30	30	30
^{b}Ln(thd)$_2^+$	40	35	41
^{b}Ln(thd)$^+$	55		8

^{a}Precursor ion. ^{b}Fragment ion.

thanide chemistry that only Eu and Yb readily form the divalent state [12]. A simple explanation of this behaviour lies in the fact that divalent Eu and Yb have exactly half-filled and filled 4f orbitals, respectively. Hence the absence of Gd(thd)$^+$ either in the mass spectrum or MS/MS spectrum is well explained.

Whilst the formation of the protonated molecules Ln(thd)$_3$H$^+$ was facile by electrospray ionization, the same was not true when using positive ion fast-atom bombardment as the method of ionization. When a liquid matrix of either glycerol or *meta*-nitrobenzyl alcohol was used with Eu(thd)$_3$, no ions relating to the complex were observed. This is in contrast to the results obtained previously for lanthanide acetylacetone complexes in negative ion made by LSIMS [1], where anionic complexes were abundantly formed. However, when an aqueous solution of Eu(thd)$_3$ was deposited directly onto the stainless steel target, positive FAB ionization produced Eu(thd)$^+$ and Eu(thd)$_2^+$ in low abundance plus Eu$^+$, EuOH and Eu$_2$O$^+$ as major ions in the spectrum. However, the molecular species were not observed. When the experiment was repeated but with acetic acid present (i.e. $Eu(thd)_3$ was dissolved in a solution containing acetic acid, then deposited onto the target), the ions $Eu(thd)^+$ and $Eu(thd)_2{}^+$ were lost, and the only ions observed other than Eu^+ and $EuOH^+$ contained either oxides or acetate ligands.

Conclusions

Electrospray ionization is a versatile technique with great potential for the study of complex ions in solution and their solution chemistry. Such studies were not possible using the ionization methods previously employed such as electron impact [10, 11] or LSIMS [1].

The electrospray mass spectra of $Ln(thd)_3$ species in a methanol/water solution containing acetic acid showed intense protonated molecules $Ln(thd)H^+$ for Ln = Eu, Gd and Yb. A great diversity of other ionic species was also observed. These mainly involved the ligands thd, acetato (AcO^-), H_2O and H^+ in a number of mixed-ligand cationic species. Eu formed complexes in the divalent state both in electrospray ionization and as a result of collisional activation of $Eu(III)(thd)_3H^+$. In contrast, Yb only formed a divalent complex as a result of collisional activation of $Yb(III)(thd)_3H^+$. Gd only formed complexes in the trivalent oxidation state. The origin of ions at 78 mass units above $Eu(thd)_2{}^+$ and $Eu(thd)^+$ (and at the corresponding position for Gd and Yb) is thought to involve protonation of a neutral complex such as $[Eu(thd)_2(AcO)(H_2O)]H^+$. It is desirable to further characterize such species by tandem mass spectrometry and work in this direction is in progress.

References

1 A. S. Plaziak, C. Zeng, C. E. Costello, S. Lis and M. Elbanowski, *Inorg. Chim. Acta, 184* (1991) 229.
2 M. Mann, *Org. Mass Spectrom., 25* (1990) 575.
3 J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong and C. M. Whitehouse, *Mass Spectrom. Rev., 9* (1990) 37.
4 C. K. Meng, M. Mann and J. B. Fenn, *Z. Phys. D, 10* (1988) 361.
5 R. D. Smith, J. A. Loo, C. G. Edmonds, C. J. Baringa and H. R. Udseth, *Anal. Chem., 62* (1990) 882.
6 R. T. Gallagher, J. R. Chapman and M. Mann, *Rapid Commun. Mass Spectrom., 4* (1990) 369.
7 F. W. McLafferty, *Interpretation of Mass Spectra,* University Science Books, Mill Valley, CA, USA, 1980.
8 C. R. Blakley and M. L. Vestal, *Anal. Chem., 55* (1983) 750.
9 M. Barber, R. S. Bordoli, G. J. Elliott, R. D. Sedgwick and A. N. Tyler, *Anal. Chem., 54* (1982) 645A.
10 S. Lis, A. S. Plaziak and M. Elbanowski, *Inorg. Chim. Acta, 155* (1989) 259.
11 M. Das and S. E. Livingstone, *Aust. J. Chem., 28* (1975) 1415.
12 T. Moeller, *The Chemistry of the Lanthanides,* Reinhold, New York, 1963.