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MASS SPECTROMETRY OF THE PARAMAGNETIC NMR SHIFT REAGENTS Eu(FOD)$_3$ AND Yb(FOD)$_3$ AND THEIR ADDUCTS WITH PROPYLAMINE

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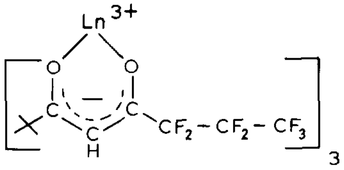
By means of electron impact mass spectrometry, the occurrence of dimeric (or higher) associates of the lanthanide shift reagents Eu(fod)$_3$ and Yb(fod)$_3$ has been demonstrated. Also, the occurrence of 1:1 and 1:2 adducts of Ln(fod)$_3$ with propylamine was shown.

Lanthanide shift reagents have become valuable tools in NMR spectroscopy.[1] First of all these reagents have found widespread use in the separation of overlapping signals in NMR spectra of organic substrates able to act as ligands. In addition, information on molecular structure can be obtained from the magnitudes of the induced shifts in the organic substrates.

The commonly used lanthanide chelates Eu(fod)$_3$ and Yb(fod)$_3$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) are rather volatile and, therefore, suitable for mass spectrometry.[2] Previously we have demonstrated the applicability of mass spectrometry in the detection of compounds of the type Ln(fod)$_3$.Mfod (M = Na, K, Rb, Cs), which were shown to be frequently present as impurities in commercial shift reagents.[3] This result encouraged us to perform some further mass-spectral investigations in this field.



First, the electron impact mass spectra of Eu(fod)$_3$ and Yb(fod)$_3$ were reinvestigated. Electron impact[2] and chemical ionization[4] mass spectra of Ln(fod)$_3$ compounds have been reported. These literature spectra showed peaks up to mass numbers corresponding with $[\mathrm{Ln(fod)_3}]^{+\cdot}$. Upon extension of the scan up to *m/z* = 2000 we detected peaks, which may be ascribed to the fragments $([\mathrm{Ln(fod)_3}]_2 - \mathrm{Hfod})^{+\cdot}$ and $([\mathrm{Ln(fod)_3}]_2 - \mathrm{Hfod} - \text{t-Bu})^{+}$ (see Figure 1). The characteristic patterns of the isotopic clusters of these peaks unambiguously show the presence of two lanthanide nuclei in the corresponding fragments: the peaks in the Eu(fod)$_3$-spectra show a 1:2:1 pattern, which is in agreement with the natural abundance of the ^{151}Eu and ^{153}Eu isotopes (47.8 and 52.2%). The presence of mass spectral fragments containing two lanthanide atoms show that *in the gas phase* dimeric (or higher) associates of Ln(fod)$_3$ occur. Apparently these self-association products are rather stable, even under mass spectrometric conditions. NMR and vapor pressure osmometric

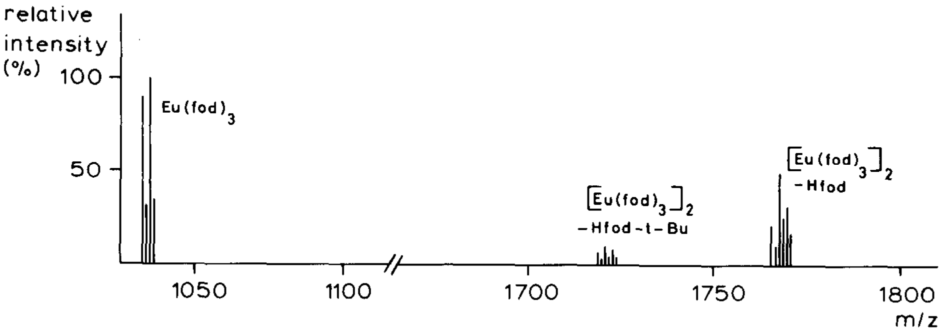


Figure 1. The electron impact mass spectrum of Eu(fod)$_3$ (70 eV).

studies have shown that self-association of Ln(fod)$_3$ chelates occur in solution.[5,6,3] Springer *et al.* have determined that the association constants for the formation of dimers and trimers of Eu(fod)$_3$ in CCl_4 at 37 °C are 367 ± 22 M^{-1} and 12 ± 2 M^{-1}, respectively.[6] Moreover, several of the related Ln(dpm)$_3$ shift reagents are known to crystallize as dimeric units through sharing of two oxygen atoms by the lanthanide ions.[7]

From NMR spectra obtained after successive addition of portions of Eu(fod)$_3$ to a solution of propylamine in $CDCl_3$ the dependence of the ^1H shifts upon ρ (the molar ratio of Eu(fod)$_3$ added/propylamine) was determined (Figure 2). From the occurrence of the maxima in these plots

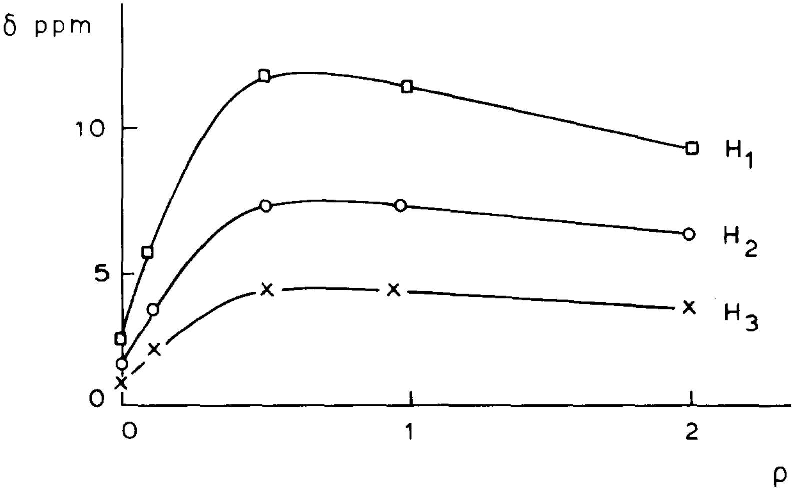


Figure 2. ^1H chemical shifts of propylamine (100 mg) in $CDCl_3$ (0.5 ml) at 60 MHz and 37° *versus* ρ (molar ratio of Eu(fod)$_3$ added/propylamine).

it may be concluded that Eu(fod)$_3$ forms 1:1 and 1:2 adducts with propylamine. From each NMR sample 5 µl was introduced in the mass spectrometer with the use of the direct insertion probe. After pumping away the solvent, mass spectra were obtained which showed, surprisingly, peaks at *m/z* 1095 and 1154, corresponding with the molecular masses of Eu(fod)$_3$.n-$C_3H_7NH_2$ and Eu(fod)$_3$.(n-$C_3H_7NH_2$)$_2$, respectively (see Figure 3). In addition, some peaks, which are due to fragmentation of these species were observed (*m/z* 1037, 1066, 1096). The trends in the intensities of these peaks are roughly in agreement with the concentration of the 1:1 and 1:2 Eu(fod)$_3$/n-$C_3H_7NH_2$ adducts in solution (see Table 1). At $\rho < 0.5$ a peak at *m/z* 1154 ([Eu(fod)$_3$(n-$C_3H_7NH_2$)$_2$]$^{+\cdot}$) shows up, the intensity of which increases at decreasing ρ-values.

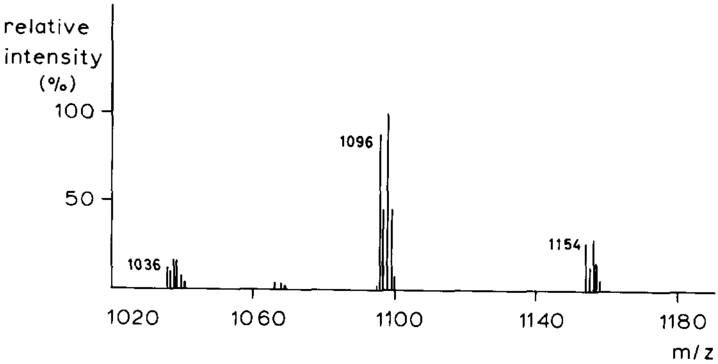


Figure 3. The electron impact mass spectrum (70 eV) of a mixture of Eu(fod)$_3$ and propylamine (ρ = 0.1).

Table 1. Relative intensities in the mass spectra (70 eV) of mixtures of Eu(fod)$_3$ and n-$C_3H_7NH_2$ at different molar ratios Eu(fod)$_3$ added/n-$C_3H_7NH_2$ (ρ).

ρ	*m/z* = 1036 [Eu(fod)$_3$]$^{+\cdot}$	*m/z* = 1037[a]	*m/z* = 1095 [Eu(fod)$_3$.n-$C_3H_7NH_2$]$^{+\cdot}$	*m/z* = 1096[a]	*m/z* = 1154 [Eu(fod)$_3$(n-$C_3H_7NH_2$)$_2$]$^{+\cdot}$
2	1700	--[b]	100	--[b]	--[b]
1	7	7	100	--[b]	--[b]
0.5	17	13	100	--[b]	2
0.2	44	77	64	100	10
0.1	6	15	1	100	35

[a] Corrected for ^{13}C natural abundance; [b] Not observable.

This is accompanied by an increase of the peak at *m/z* 1096, which is probably due to loss of $C_3H_8N^{\cdot}$ from the parent $[Eu(fod)_3(n\text{-}C_3H_7NH_2)_2]^{+\cdot}$. At $\rho = 2$, the peak at *m/z* 1036 ($[Eu(fod)_3]^{+\cdot}$) predominates. The irregularities present in the intensities as function of ρ (Table 1) are probably due to differences in volatility between the various complexes, which results in some dependence of the relative intensities on the time between the introduction of the sample in the mass spectrometer and the measurement of the spectrum.

Analogous phenomena were observed with $Yb(fod)_3$. However, in this case in addition a peak at *m/z* 1195 $(Yb(fod)_3(n\text{-}C_3H_7NH_2)_2 + 18)^{+\cdot}$ was observed. This peak might be ascribed to the adduct $Yb(fod)_3(n\text{-}C_3H_7NH_2)_2\ H_2O$. Coordination numbers of 9 are not uncommon for lanthanides, but as far as we know, this is the first observation of a $Ln(fod)_3$ reagent coordinated with 3 additional ligands.

It may be concluded that mass spectrometry seems to be a useful tool for the investigation of relatively stable adducts of lanthanide shift reagents with organic substrates. Other examples are under investigation.

Acknowledgements

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