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ISOTOPE EFFECTS IN NUCLEAR MAGNETIC RESONANCE SPECTRA OF POLYGLYCOLDIMETHYLETHERS, COMPLEXED WITH RARE-EARTH SHIFT REAGENTS.

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Recently (1,2) we observed an interesting isotope effect in the NMR spectrum of $CH_3OCH_2CD_2OCH_2\overset{1}{C}H_2O\overset{2}{C}H_2\overset{3}{C}H_2OCH_3$ (d_2-glyme-4) complexed with tris(dipivalomethanato)europium ($Eu(DPM)_3$) (3) or -praseodymium ($Pr(DPM)_3$) (4) . All lines, detected in the spectrum of the non-deuterated glyme-4 lanthanide (Ln) complex, were doubled in the spectrum of the deuterated d_2-glyme-4 lanthanide complex (see ref. 1, fig. 2 and fig. 5). Smith et al. (5) also reported such an effect for the adducts formed by complexation of $Eu(DPM)_3$.2 pyridine to deuterated and non-deuterated trans-verbanol. They explained this phenomenon by a greater association constant between the deuterium substituted compound and the metal complex than between the non-deuterated compound and the metal complex. In this paper we like to present further evidence for the correctness of this interpretation . We will show that the isotope effect, observed in the spectra of $Ln(DPM)_3$-d_2-glyme-4, is caused by an intramolecular exchange reaction of the lanthanide complex. Furthermore we will demonstrate that in the spectra of $Ln(DPM)_3$, complexed with a mixture of non-deuterated glyme-5 and symmetrically deuterated d_4-glyme-5 ($[CH_3OCH_2CH_2OCD_2CH_2]_2O$), intermolecular exchange reactions of the lanthanide complex give rise to isotope effects, similar to those observed in the spectra of $Ln(DPM)_3$-d_2-glyme-4.

Intramolecular exchange

A spectrum of a solution containing equivalent amounts of $Pr(DPM)_3$ and d_2-glyme-4 in CCl_4 has been given in an earlier publication (1, fig. 5). Compared with the NMR pattern of $Ln(DPM)_3$ with non-deuterated glyme-4, which consists of one singlet for the CH_3 group and two unresolved triplets and one singlet for the CH_2 groups (1, fig. 2), the spectrum of $Pr(DPM)_3$-d_2-glyme-4 clearly shows a doubling of the CH_3, C_3 and C_1 signals, the shift difference between the two methyl peaks being 19Hz. However, in the NMR spectrum of a solution of d_2-glyme-4 in the presence of a 2.5 times excess of $Pr(DPM)_3$, this doubling was absent.

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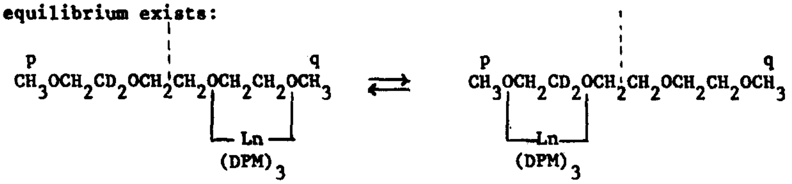
We already pointed out (2) that in an Ln(DPM)$_3$-d$_2$-glyme-4 (1 : 1) mixture the following equilibrium exists:



$$\overset{p}{CH_3}OCH_2CD_2OCH_2CH_2OCH_2CH_2O\overset{q}{CH_3} \rightleftarrows \overset{p}{CH_3}OCH_2CD_2OCH_2CH_2OCH_2CH_2O\overset{q}{CH_3}$$

(A) (B)

In the fast exchange limit the recorded NMR spectrum will be a statistical average of the spectra of A and B.

If the complexation constant between the metal complex and the -OCH$_2$CD$_2$O- moiety is greater than between the metal complex and the -OCH$_2$CH$_2$O- moiety a doubling of all NMR signals will occur because of this exchange reaction (except for the C$_2$ peak). The most shifted peak of each couple arises from those protons, situated in that half of the molecule which contains the CD$_2$ group[x]. As reported before (2), when the lanthanide/glyme ratio exceeds unity, a second lanthanide complex binds to the glyme. In this situation the intramolecular reaction is blocked and the doubling of the peaks must disappear, as has in fact been observed.

The equilibrium constant K for this exchange reaction may be obtained in the following way. In the fast exchange limit the resonances of, for instance, the two CH$_3$ groups, indicated by $\bar{\omega}_p$ and $\bar{\omega}_q$ (see reaction scheme), are given by

$$\bar{\omega}_p = f_A\omega_A + f_B\omega_B$$

$$\bar{\omega}_q = f_B\omega_A + f_A\omega_B$$

where f_A and f_B are the fractions of species A and B, respectively, ω_A is the resonance frequency of the methyl group p in species A ($\equiv$ resonance frequency of the methyl group q in species B), and ω_B is the resonance frequency of the methylgroup p in species B ($\equiv$ resonance frequency of the methyl group q in species A).

Since $K = f_B/f_A$, it is easy to show that

$$K = \frac{(\omega_A - \omega_B) + (\bar{\omega}_q - \bar{\omega}_p)}{(\omega_A - \omega_B) - (\bar{\omega}_q - \bar{\omega}_p)}$$

$(\bar{\omega}_q - \bar{\omega}_p)$ can be measured directly from the spectra of the Ln(DPM)$_3$-d$_2$-glyme-4 (1 : 1) mixtures. A good estimate for ω_A and ω_B can be obtained from the spectrum of a 1 : 1 mixture of Ln(DPM)$_3$ and ethyleneglycol methyl, n-octylether (CH$_3$OCH$_2$CH$_2$O(CH$_2$)$_7$CH$_3$), a compound containing one complexation site of two oxygen atoms. This results in a value for K of 1.030 ± 0.005 for both Eu(DPM)$_3$ and Pr(DPM)$_3$, which seems to be a reasonable value for such an isotope effect.

[x] This can be derived from the two peaks originating from the C$_3$ protons (see fig. 5, ref. 1). The peak with the smallest linewidth is shifted most. Since the linewidth is mainly determined by the spin-spin interactions with the neighbouring group, the narrowest peak must be assigned to the CH$_2$ group adjacent to the CD$_2$ group.

Intermolecular exchange

Another system, which has been investigated by us is a mixture of glyme-5 and d_4-glyme-5, glyme-5 being present in slight excess. A solution of a small amount of this mixture in CCl_4 with a 2.5 times excess of $Eu(DPM)_3$ yields the NMR pattern, shown in figure 1.

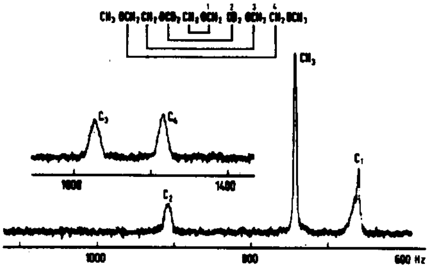


Fig. 1. ^1H NMR spectrum (60 MHz) of a 2.5 : 1 mixture of $Eu(DPM)_3$ and glyme-5/d_4-glyme-5 (glyme-5 in slight excess) in CCl_4 at 37°C ([$Eu(DPM)_3$] = 0.15 M). Peak positions are given relative to TMS.

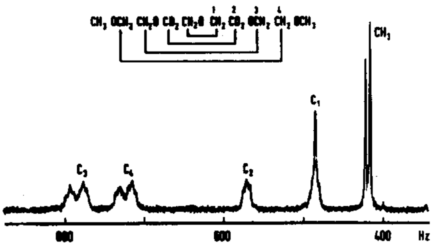


Fig. 2. ^1H NMR spectrum (60 MHz) of a 1 : 1 mixture of $Eu(DPM)_3$ and glyme-5/d_4-glyme-5 (glyme-5 in slight excess) in CCl_4 at 37°C ([$Eu(DPM)_3$] = 0.15 M). Peak positions are given relative to TMS.

The structural formula of the deuterated species is given in this figure, together with the peak assignments, which were reported before (2). The spectrum shows one set of NMR signals and is almost identical to that of $Eu(DPM)_3$ and non-deuterated glyme-5 (ratio 2.5 : 1). However, the same mixture but with a $Eu(DPM)_3$ concentration equal to the total glyme concentration (ratio 1 : 1) gives rise to the NMR pattern, shown in figure 2.

Now the CH_3, C_3 and C_4 signals are doubled. The most shifted member of each couple, having the lowest intensity, must be assigned to the deuterated glyme-5, in accordance with our earlier findings that deuteration enhances the association constant between the rare earth complex and the glyme oxygens.

This observation can not be explained by intramolecular exchange because of the symmetry of the glyme molecules involved. One is forced to postulate the presence of a small percentage of diassociated lanthanide/glyme adduct ($[Ln(DPM)_3]_2$-glyme) in the 1 : 1 mixture of lanthanide and glyme-5/d_4-glyme-5. The stronger binding of $Ln(DPM)_3$ to the deuterated species than to the non-deuterated species leads to a slight excess of $[Ln(DPM)_3]_2$-d_4-glyme-5 with respect to $[Ln(DPM)_3]_2$-glyme-5. Intermolecular Ln exchange reactions between the various species, e.g. mono- and diassociated lanthanide/glyme complexes, will then produce the extra set of peaks, observed in the spectrum which is shown in figure 2. This explanation is supported by the observation that the chemical shift differences disappear when the Ln/total glyme ratio is 2.5 : 1 (fig. 1).

It is tempting to speculate about the origin of these kinetic isotope effects. The observed effects seem to indicate that not only the oxygen atoms are involved in the binding of the metal complex, but also some protons (deuterons). This view is supported by the observation that the shifts of the protons of the terminal and penultimate CH_2 groups not only originate from contributions of pseudo-contact interactions but also contain a Fermi contact shift contribution (2).

The experiments were performed on a Varian A60A and a Varian T60 spectrometer.

Acknowledgement

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