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LANTHANIDE-INDUCED CONTACT SHIFTS IN POLYGLYCOLDIMETHYLETHERS

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Complexation of polyglycoldimethylethers (glymes) of the general formula $CH_3(CH_2CH_2O)_nCH_3$ with certain aromatic radical ion salts such as coronene sodium is known to result in strong downfield nuclear magnetic resonance shifts of the glyme protons (1,2). The shifts, amounting to as much as 12 ppm and interpreted in terms of a Fermi contact mechanism, produce a first order spectrum for the CH_2 protons, each peak representing a combination of two or more CH_2 groups.

The large proton nmr shifts recently reported for many organic compounds in the presence of paramagnetic lanthanide complexes such as tris(dipivalomethanato) europium and -praseodymium (3-9) induced us to look at mixtures of these lanthanide shift reagents with the polyfunctional glymes. In the actual experiments, small quantities of glyme (some of them partially deuterated) with n ranging from 1 to 6 were added to a 0.15 M solution of a lanthanide complex in CCl_4, and the nmr spectra recorded on a Varian A60A spectrometer. In a number of experiments the molar ratio of lanthanide to glyme was varied from 0.2 to 4.0

The spectra of the 1:1 glyme-Eu adducts reveal a sharp peak representing the two terminal CH_3 groups, and further downfield a series of well resolved absorptions each representing two CH_2 groups. Addition of more glyme yields a rapid exchange spectrum, and plots of the proton shifts versus the ratio of the concentration of the 1:1 adduct to that of total glyme are linear and passing

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through the origin, implying that at 0.15 M of the 1:1 mixture essentially all of the glyme is bound to the $Eu(dpm)_3$.

It is interesting that the spectrum of a glyme 5/$Eu(dpm)_3$ mixture (the number following the glyme refers to the number of oxygen atoms in the glyme) clearly exhibits four triplets, each representing a combination of two CH_2 groups. For a similar mixture with glyme 4 one of the $CH_2...CH_2$ peaks is a singlet. Glyme 3 shows two triplets, while a glyme 6/$Eu(dpm)_3$ spectrum consists of four well resolved triplets and a singlet, in addition to the CH_3 group. Apparently, the two CH_2 groups representing one nmr absorption are equally far removed from the center of the molecule. Using glyme 4 as an example:

$$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$$

(3)(2) (1)(1) (2)(3)

the C_1 protons will give a singlet, while triplets are expected for the C(2) and C(3) protons. Glymes with an odd number of oxygen atoms (glyme 3 or 5) yield only triplets.

The following deuterated glymes were prepared for further peak assignments: $(CH_3OCH_2CH_2OCD_2CH_2)_2O$, $(CH_3OCH_2CD_2OCH_2CH_2)_2O$ and $CH_3OCH_2CD_2OCH_2CH_2OCH_2CH_2OCH_3$. These compounds were sufficient to assign all glyme 4 and glyme 5 absorptions, since the CH_2 protons adjacent to a CD_2 group are changed from a triplet to a singlet. Also, some interesting isotope effects on the chemical shifts were found, with the CH_3 absorption splitting up in a doublet for the asymmetrically deuterated glyme 4 (20 cps peak separation with Pr).

The respective chemical shifts are listed in Table I, all values being relative to the chemical shifts of the glyme protons in pure glyme. Results obtained with praseodymium $(dpm)_3$ are also included. The most striking observation concerns the Pr/Eu shift ratio for the various glyme protons. For the two 1:1 lanthanide-glyme 4 complexes the Pr/Eu shift ratio is 3.0 for the CH_3 group and 3.2 for the C(1) protons. However, the ratios are only 1.9 for the C(2) protons and 1.7 for the C(3) protons. A similar behavior is observed for glyme 5, with the respective Pr/Eu shift ratios being 2.9, 3.0 and 2.9 for the CH_3, C(1) and C(2) protons, and only 1.9 and 1.7 for the penultimate CH_2 (C3) and terminal CH_2(C4) groups. These data suggest that it is not always

Table I

Proton NMR Shifts of Glyme 4 and Glyme 5 Adducts of $Eu(dpm)_3$ and $Pr(dpm)_3$ in CCl_4 at 40°C, relative to the Chemical Shifts of Non Complexed Glyme (both measured with respect to TMS). Concentration of Paramagnetic Complex:0.15 M.

Mixture	CH_3	C(1)	C(2)	C(3)	C(4)
Eu/G4 = 1:0.2	-567	-521	-1253	-1215	
Eu/G4 = 1:1	-253	-385	-617	-562	
Eu/G4 = 1:2	-124	-212	-318	-282	
Pr/G4 = 1:0.2	1541	2120	2065	2011	
Pr/G4 = 1:1	763	1251	1200	977	
Pr/G4 = 1:2	373	635	599	497	
Eu/G5 = 1:1	-208	-256	-335	-519	-465
Pr/G5 = 1:1	604	767	965	965	809

justified to convert proton shifts obtained for one complex into those for another lanthanide complex by applying a constant shift ratio factor (8,9). Our tentative conclusion is that the Eu or Pr ion is chelated predominantly to the outer two oxygen atoms of the glyme chain, bringing the two CH_2 groups connecting these two oxygen atoms in close proximity to the paramagnetic ion. This apparently results in a considerable Fermi contact shift on these protons, in addition to the expected dipolar shift. Both kinds of shift are downfield for the Eu-glyme adduct, but they are in opposite direction for the Pr complex. The combined effects lead to the low shift ratios found for these protons.

Supporting evidence for the simultaneous binding of two glyme oxygen atoms to Eu or Pr is found in the behavior of ortho and meta-dimethoxybenzene. The CH_3 protons of the ortho compound in a 1:1 mixture with $Eu(dpm)_3$ are shifted to the same extent as found for 1,2 dimethoxyethane, while the CH_3 shift for the meta derivative is concentration dependent and, at 0.15 M, amounts to only about 1/5 of that of the ortho compound. Also, 1,2 dimethoxyethane is much stronger bound to $Eu(dpm)_3$ than ethers with one oxygen atom, including tetrahydrofuran.

The nmr patterns of the glyme adducts (e.g., the identical shifts of CH_2 groups equally far removed from the center of the glyme molecule) suggest a rapid intramolecular exchange of the lanthanide reagent between $-OCH_2CH_2O-$ moieties on opposite ends of the chain and/or an intermolecular exchange between complexed glyme molecules. Also, when the lanthanide/glyme ratio exceeds unity, a second paramagnetic complex binds to the glyme (not observed for DME), causing an even further shift of the glyme protons (See Table 1). Additional work on these interesting chelating systems are in progress in order to compare their behavior with that found for the radical anion shift reagents.

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