

LANTHANIDE-INDUCED CONTACT SHIFTS IN POLYGLYCOLDIMETHYLETERS
V ADDITIVITY OF THE SHIFTS⁺

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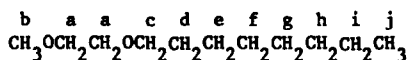
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Recently Ius et al. (1) investigated the effect of $\text{Eu}(\text{DPM})_3$ (2-3) on the NMR spectrum of a solution of the bifunctional compound 17-carbomethoxy-methylene-5-androsten-3 β -ol in CDCl_3 . They found that the contributions to the lanthanide induced (LI) shift for each proton in this compound due to coordination of $\text{Eu}(\text{DPM})_3$ at the two functional groups are additive. We like to present here a few more examples supporting this additivity rule, viz. $\text{Eu}(\text{DPM})_3$ (2-3) and $\text{Pr}(\text{DPM})_3$ (4) complexed to various polyglycoldimethylethers (glymes). In Part I we pointed out that the glyme molecules are coordinated to the Ln complexes with two oxygen atoms at the time (coordination number of Ln = 8). Glyme-6 (see Fig. 2), for instance, has five different coordination sites, each consisting of two oxygen atoms. For the calculation of the shifts in the 1 : 1 Ln-glyme complexes we have chosen 2, 5-dioxatridecane



as a standard compound. Because there is only one pair of oxygen atoms present in this compound, the place of coordination of the lanthanide complex to the ether is definitely established. The NMR spectrum of $\text{Pr}(\text{DPM})_3$, 2,5-dioxatridecane (1 : 1) in CCl_4 is shown in figure 1 and in table 1 the shifts of the peaks for the ether protons have been given for both the Eu and the Pr complex. Using these data the shifts for the glyme protons in the $\text{Ln}(\text{DPM})_3$, glyme (1 : 1) adducts are calculated in the following way. Let us consider glyme-6. Since the NMR spectra of the $\text{Ln}(\text{DPM})_3$, glyme adducts point to the presence of a two fold symmetry in the complex (see Part I and ref. 5), the following coordination structures must be considered:

⁺) Part I and II appeared earlier in Tetrahedron Letters, 4863 (1971) and 2067 (1972)

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Table 1

Glyme proton shifts of the 1 : 1 adducts of 2,5-dioxatridecane with $\text{Eu}(\text{DPM})_3$ and $\text{Pr}(\text{DPM})_3$ in CCl_4 at 40°C ($\text{Ln}(\text{DPM})_3 = 0.15 \text{ M}$). The shifts are relative to non complexed 2,5-dioxatridecane.

Adduct	δ (ppm)									
	C_a	$(\text{CH}_2)_b$	C_c	C_d	C_e	C_f	C_g	C_h	C_i	$(\text{CH}_2)_j$
Eu-ether (1 : 1)	19.8	8.8	7.9	4.4	1.82	0.83	0.17	0.17	0.17	0
Pr-ether (1 : 1)	-32.1	-25.2	-27.9	-13.8	-7.1	-3.6	-1.78	-1.05	-0.70	-0.28

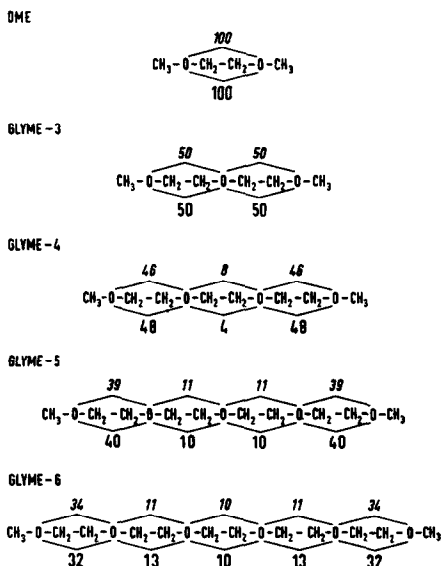


Fig. 2: Complexation of glymes to $\text{Eu}(\text{DPM})_3$ (italics) and $\text{Pr}(\text{DPM})_3$ in percentages from calculations with 2,5-dioxatridecane as a standard compound.

Results of calculations for $\text{Pr}(\text{DPM})_3$, glyme-6 (1 : 1), according to the described method, together with the experimental glyme shifts have been given in table 2. As can be seen from this table a quite reasonable fit between calculated and experimental LI glyme shift values is obtained. This proves that the contributions to the LI shift for each proton in a certain glyme due to complexation of $\text{Ln}(\text{DPM})_3$ at the several coordination sites within that glyme, are additive.

Table 2

Calculated and experimental glyme proton shifts for $\text{Pr}(\text{DPM})_3$, glyme-6 (1 : 1) in CCl_4 at 40°C ($[\text{Pr}(\text{DPM})_3] = 0.15 \text{ M}$). All shifts are relative to non complexed glyme.

	CH_3	C_1	C_2	C_3	C_4	C_5
$-\delta_{\text{I}}^{\text{i}}$ (ppm)	12.6	2.7	7.2	14.1	16.1	16.1
$-\delta_{\text{II}}^{\text{i}}$ (ppm)	1.8	20.8	17.8	16.9	14.3	7.0
$-\delta_{\text{III}}^{\text{i}}$ (ppm)	0.70	32.1	27.9	13.8	3.6	1.78
$-\delta_{\text{calc}}^{\text{i}}$ (ppm)	8.6	10.4	12.1	14.8	14.4	12.3
$-\delta_{\text{exp}}^{\text{i}}$ (ppm)	9.1	11.3	11.9	14.8	14.8	12.3

The calculated weight factors for a number of 1 : 1 $\text{Ln}(\text{DPM})_3$, glyme adducts have been shown in figure 2. It gives an interesting impression of the coordination preference of $\text{Ln}(\text{DPM})_3$ to a long molecule chain, with many oxygen atoms. Though the basis for these calculations is not ideal, it is gratifying that the weight factors for 1 : 1 $\text{Eu}(\text{DPM})_3$, glyme and comparable 1 : 1 $\text{Pr}(\text{DPM})_3$, glyme adducts are almost equal.

The lanthanide complex clearly shows preference for complexating at the ends of the glyme chain. When binding to a $\text{Ln}(\text{DPM})_3$ complex a glyme molecule apparently prefers having one short and one long loose end, rather than having two medium long ends, probably because of more sterical hindrance with the DPM ligands in the latter case.

The experiments were performed on a Varian A60A spectrometer operating at 60 MHz. The 2,5-dioxatridecane was prepared, following a procedure of Berggärth (6).

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