

LANTHANIDE-INDUCED CONTACT SHIFTS IN POLYGLYCOLDIMETHYLETERS

IV CHEMICAL EXCHANGE\*

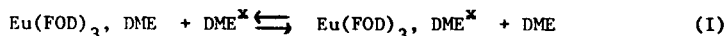
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Recently Evans and Wyatt (1) observed slow exchange in the NMR spectra of a mixture of  $\text{Eu}(\text{FOD})_3$  (2) and excess of dimethyl sulphoxide (DMSO) in  $\text{CD}_2\text{Cl}_2$ . At  $-80^\circ\text{C}$  they observed peaks for both free and complexed DMSO. In this paper we report a few more cases of slow exchange in the NMR spectra of mixtures of lanthanide (Ln) complex and polyglycoldimethyl-ether (glyme) in  $\text{CDCl}_3$  at low temperatures. For the case of  $\text{Eu}(\text{FOD})_3$ , dimethoxyethane (1 : 2) we also present the thermodynamic exchange parameters, obtained by simulation of the experimental spectra

Fig. 1 shows the temperature behaviour of the NMR spectrum of a 1 : 2 mixture of  $\text{Eu}(\text{FOD})_3$  and dimethoxyethane (DME) in  $\text{CDCl}_3$ . At  $+31.5^\circ\text{C}$  (spectrum a) one single NMR pattern is obtained for free and complexed DME, consisting of two relatively sharp singlets for the  $\text{CH}_3$  and  $\text{CH}_2$  protons of DME, respectively. Apparently the equilibrium



is fast on the NMR time scale. Lowering the temperature causes severe broadening of the DMF signals, as can be seen from spectrum b at  $-14.5^\circ\text{C}$ . When the temperature is decreased further an extra peak appears, shown by spectrum c at  $-43.5^\circ\text{C}$ . Finally at  $-62.5^\circ\text{C}$  (spectrum d) the NMR signals are sharp again. At this temperature the resonance positions of the  $\text{CH}_2$  and  $\text{CH}_3$  protons of complexed DME are equal to the resonance positions of these protons in the 1 : 1 complex ( $\text{Eu}(\text{FOD})_3, \text{DME}$ ) measured also in  $\text{CDCl}_3$  at  $-62.5^\circ\text{C}$ . The position of the extra peak corresponds to the resonance positions of the protons in free DME. The intensity ratio of the peaks of free and complexed DME is approximately 1 : 1. Apparently at  $-62.5^\circ\text{C}$  equilibrium I is completely frozen out on the proton resonance time scale (slow exchange limit).

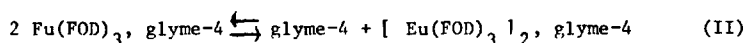
+ ) Part I and II appeared earlier in Tetrahedron Letters, 4863 (1971), 2067 (1972), respectively. For part III see preceding paper.

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All NMR spectra have been simulated by using the modified Bloch equations describing exchange between two equally populated sites (3). The simulation requires three independent parameters only, viz. the linewidths of the various NMR signals in the absence of exchange, the life time  $\tau$  of a particular configuration and the positions of the peaks at conditions of very slow exchange ( $\tau \rightarrow \infty$ ). The linewidths of the peaks in the absence of exchange were obtained by measuring the 1:1 complex  $\text{Eu}(\text{FOD})_3$ , DME in  $\text{CDCl}_3$  at various temperatures. The resonance positions of the proton peaks in the NMR spectrum of the 1:1 complex were determined from a mixture containing the Ln complex in slight excess. The lifetime  $\tau$  at a given temperature was found by trial and error: it was varied until the complete pattern of the simulated NMR spectrum matched perfectly with that of the experimental spectrum. The computer simulations for the spectra at  $-14.5^\circ\text{C}$  (b) and  $-43.5^\circ\text{C}$  (c) are represented by the smooth lines in fig. 1. The Arrhenius plot for equilibrium I is shown in fig. 2. From this plot we estimated an activation energy of  $10 \pm 0.5 \text{ kcal mol}^{-1}$  and a frequency factor of  $3 \times 10^{13} \text{ (l mol}^{-1} \text{ sec}^{-1})$ . Application of the Eyring equation resulted in values for the thermodynamic constants of the activated complex  $\Delta G^\ddagger = +10.5 \pm 1.0 \text{ kcal mol}^{-1}$ ,  $\Delta H^\ddagger = +9.5 \pm 0.5 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -4 \pm 2 \text{ e.u.}$

Among the other systems investigated,  $\text{Pr}(\text{FOD})_3$ , DME (1:2) in  $\text{CDCl}_3$  (2),  $\text{Eu}(\text{DPM})_3$ , DME (1:2) in  $\text{CDCl}_3$  (4-5) and  $\text{Pr}(\text{DPM})_3$ , DME (1:2) in  $\text{CDCl}_3$  (6) all showed a slow exchange NMR pattern at  $-62.5^\circ\text{C}$ , e.g. separate peaks could be observed for free and complexed DME with an intensity ratio of 1:1. For the  $\text{Eu}(\text{DPM})_3$ , DME and  $\text{Pr}(\text{DPM})_3$ , DME systems this is a rather surprising result in view of the much smaller complexation constant of DME to  $\text{Ln}(\text{DPM})_3$  complexes ( $\approx 10^3 \text{ l mol}^{-1}$ ) compared to  $\text{Ln}(\text{FOD})_3$  complexes ( $\approx 10^5 \text{ l mol}^{-1}$ ).

In an attempt to measure the exchange reaction also for other members of the polyglycol-dimethylethers we studied the complexes of  $\text{Eu}(\text{FOD})_3$ , glyme-4 (the number behind the word glyme indicates the number of oxygen atoms in the glyme). An unexpected result was obtained for the 1:1 complex in  $\text{CDCl}_3$ . Upon lowering the temperature severe broadening of the four proton peaks of glyme-4 (see ref. 7) took place. At  $-62.5^\circ\text{C}$  these peaks were sharp again, but surprisingly the spectrum contained an extra peak at the field position where the protons in free glyme-4 resonate. It appeared that at  $-62.5^\circ\text{C}$  the positions of the peaks of complexed glyme were identical to the positions of the peaks of the protons of glyme-4, complexed to two Ln molecules and that the intensity ratio of the peaks of free to complexed glyme-4 is 1:1. Apparently we are dealing with the following equilibrium



which shifts to the right on decreasing the temperature.

The existence of 2:1 Ln-glyme-4 complexes in mixtures containing excess of Ln complex has been proven before (part I). That they can be formed also in 1:1 mixtures of Ln to glyme at low temperatures is interesting and is probably caused by entropy factors.

The NMR spectra of Ln-glyme complexes in the ratio 1:2 are rather complicated by the simultaneous occurrence of reaction equilibria of type I and II

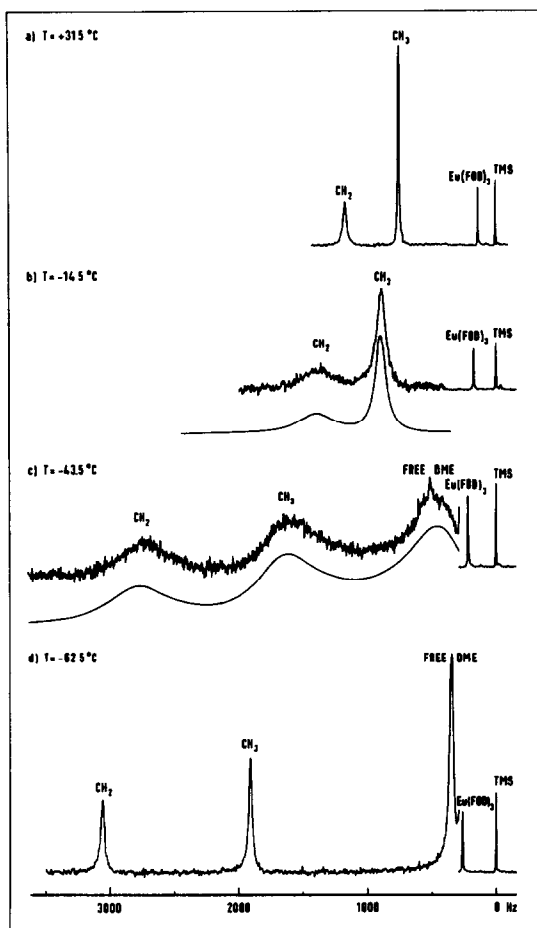


Fig. 1. A few representative spectra (100 MHz) for a 1 : 2 mixture of  $\text{Eu}(\text{FOD})_3$  and DME in  $\text{CDCl}_3$  ( $[\text{Eu}(\text{FOD})_3] = 0.075 \text{ M}$ ) at various temperatures. The smooth lines in the spectra b and c represent computer simulations.

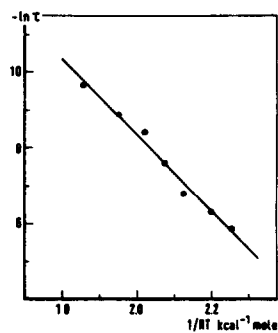


Fig. 2. Arrhenius plot for the equilibrium I in a 1 : 2 mixture of  $\text{Eu}(\text{FOD})_3$  and DME in  $\text{CDCl}_3$  ( $[\text{Eu}(\text{FOD})_3] = 0.075 \text{ M}$ ). The lifetime of a particular configuration,  $\tau$ , is given in seconds.

The  $^1\text{H}$  NMR spectra were recorded on a Varian XL 100 spectrometer operating at 100 MHz. The temperatures were measured by means of a thermocouple, placed in the rotating sample tube and connected to an electronic temperature meter. The computer simulations have been calculated on an IBM 360/50 computer.

## REFERENCES

1. D.F. Evans and M. Wyatt, Chem. Comm., 312 (1972)
2. R.E. Rondeau and R.E. Sievers, J. Amer. Chem. Soc., 93, 1522 (1971)
3. J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, New York, 1959, chapter X.
4. C.C. Hinckley, J. Amer. Chem. Soc., 91, 5160 (1969)
- 5) J.K.M. Sanders and D.H. Williams, Chem. Comm., 422 (1970)
- 6) J. Briggs, G.H. Forst, F.A. Hart, G.P. Moss and M.L. Staniforth, Chem. Comm., 749 (1970)
- 7) A.M. Grotens, J. Smid and E. de Boer, J. Magn. Res., 6, 612 (1972)