Direct Observation of Free and Complexed Substrate in a Lanthanide Shift Reagent System

By D. F. Evans* and M. Wyatt
(*Inorganic Chemistry Laboratories, Imperial College, London* SW7 2AY)

Summary The ^1H n.m.r. spectra of mixtures of tris-(1,1,1,-2,2,3,3-heptafluoro-7,7-[$^2H_6$]dimethyl[$^2H_3$]octane-4,6-dionato)europium and excess of dimethyl sulphoxide in CD_2Cl_2 have been determined over a range of temperatures; chemical exchange is slow at −80 °C and each mol of shift reagent is found to co-ordinate 2·0 ± 0·2 mol of dimethyl sulphoxide, corresponding to a co-ordination number of 8 for the europium ion.

Lanthanide 'shift reagents' have been widely used to simplify the ^1H n.m.r. spectra of complex molecules containing a co-ordinating site.[1] However, in all cases so far reported, chemical exchange between the free and complexed substrate has been fast on a proton resonance time scale. We report an example where this exchange has been slowed down, and hence the 'bound' chemical shift and the solvation number of the shift reagent can be directly determined. The Figure shows the ^1H n.m.r. spectrum of a mixture of tris-(1,1,1,2,2,3,3-heptafluoro-7,7-[$^2H_6$]dimethyl-[$^2H_3$]octane-4,6-dionato)europium, compound (**1**), and excess of dimethyl sulphoxide (Me_2SO) in CD_2Cl_2 at various temperatures. At 38 °C, a single sharp line is obtained for the Me_2SO resonance. On cooling to −45 °C this broadens, and finally at −80 °C two lines are obtained, separated by 3·42 p.p.m., which arise from complexed and free Me_2SO respectively. From the relative areas of the two peaks it is found that each mol of shift reagent complexes 2·0 ± 0·2 mol of Me_2SO, corresponding to a co-ordination number of 8 for the europium ion. The i.r. spectrum of (**1**) in CH_2Cl_2 in the region 2000—1400 cm^{-1} is almost unaffected by the addition of excess of Me_2SO, indicating that the β-diketone ligands are still bidentate. The average solvation number *n* can also be determined from the proton resonance shifts of Me_2SO-(**1**) mixtures in the temperature region where rapid chemical exchange occurs, since the 'bound' chemical shift and its temperature dependence are known.

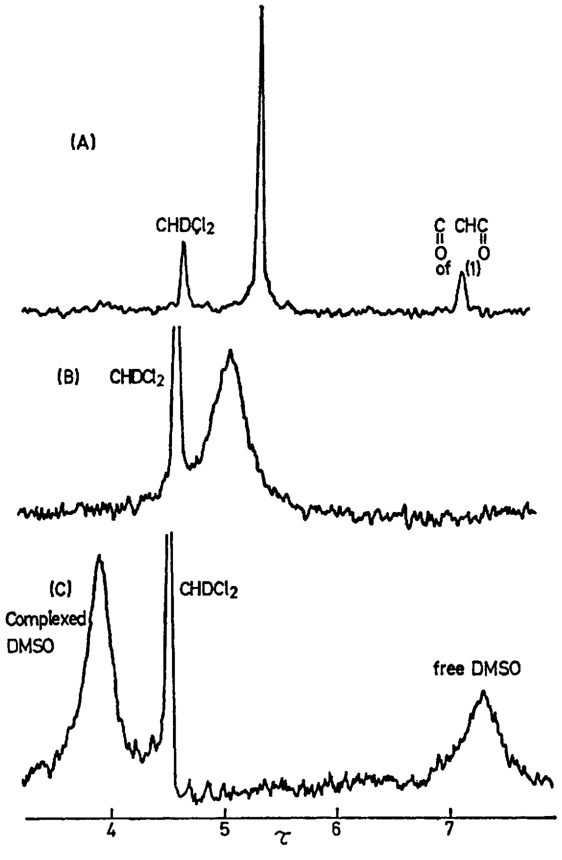

Figure ^1H *n.m.r. spectra* (*Varian HA*-100) *of* 0·044M-*solution of* (**1**) *and* 0·131M-Me_2SO *in* CD_2Cl_2 *at* A, 38°; B − 45°; *and* C, −80 °C. At −45 °C *and* −80 °C, *the resonance of* (**1**) *has moved to higher applied fields, and lies out of the region of interest.*

If the shift reagent–Me_2SO complex is essentially undissociated (as indicated by the absence of any change in δ on dilution) then δ is given by equation (1), where δ is the Me_2SO chemical shift in the rapid exchange region, δ_c is the extrapolated shift of the co-ordinated Me_2SO, δ_f is the chemical shift of the free Me_2SO and m is the number of mol of Me_2SO per mol of shift reagent. The values of n obtained in this way lie in the range 1·8—2·0.

$$\delta = \frac{\delta_c \times n}{m} + \frac{\delta_f(m - n)}{m} \qquad (1)$$

The line shapes observed at −80 °C for solutions containing various ratios of the two components indicate that chemical exchange occurs predominantly by a 'dissociative' mechanism, (*cf.* Eaton and Zaw's results for Co^{II} complexes of thiourea).[2]

Chemical exchange was much faster in the tris(dipivalomethanato)europium–Me_2SO system, possibly because of the weaker acceptor properties of this shift reagent.[3]

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[1] *E.g.* see C. C. Hinckley, *J. Amer. Chem. Soc.*, 1969, **91**, 5160; J. K. M. Sanders and D. H. Williams, *ibid.*, 1971, **93**, 641.

[2] D. R. Eaton and K. Zaw, *Canad. J. Chem.*, 1971, **49**, 3315.

[3] R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 1971, **93**, 3281.