Nuclear Magnetic Resonance Studies of Lanthanide Complexes. Part I. Solvation Numbers and Kinetics of Substrate Exchange in Lanthanide Shift Reagent Systems [1]

By **Dennis F. Evans** * and **Michael Wyatt**, Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY

Proton resonance spectra are reported for a variety of lanthanide shift reagents with four different substrates, dimethyl sulphoxide, hexamethylphosphoramide, tetramethylurea, and triethylamine. At low temperatures substrate exchange is slow on a proton resonance time-scale. Solvation numbers and bound chemical shifts were derived. In some cases the solvation numbers are solvent dependent. For many systems, quantitative kinetic data were obtained.

LANTHANIDE shift reagents are normally of the form $Ln(RCO{\cdot}CH{\cdot}COR')_3$,* where Ln is a paramagnetic lanthanide ion. In the most commonly used reagents Ln = Eu or Pr, and $R = R' = Bu^t$ [2] or alternatively $R = Bu^t$ and $R' = C_3F_7$.[3] They have been widely used to simplify the n.m.r. spectra of molecules containing a co-ordinating site.[4,5] This simplification results from the large paramagnetic shifts (in most cases predominantly pseudocontact in origin) which are induced in the co-ordinated substrate molecule. However, chemical exchange between free and complexed substrate has almost invariably been rapid on an n.m.r. time-scale. The aim of the present work was to study the proton resonance spectra of systems where this exchange could be slowed down. The main results which can be obtained under these conditions are the solvation number of the shift reagent, the bound chemical shift (δ) of the substrate molecule and, in particular, the kinetics of substrate exchange. There is little information available at present concerning the rates of ligand exchange in high co-ordination number complexes.[6]

EXPERIMENTAL

Reagents and Handling Techniques.—The reagents * $Pr(dpm)_3$ and $Eu(dpm)_3$ were obtained from B.D.H. Limited, $Pr(fod\text{-}d_9)_3$ and $Eu(fod\text{-}d_9)_3$ from Nuclear Magnetic Resonance Limited, $Eu(hfc)_3$ from Willow Brook Labs., and $Eu(tfc)_3$ from Aldrich Chemical Co. Limited. Other $Ln(fod\text{-}d_9)_3$ and $Ln(fhd)_3$ shift reagents were prepared from the appropriate β-diketonate following the method of Springer *et al.*[7] Since water co-ordinates strongly to the shift reagents,[5] they were freshly dehydrated at 100 °C [80 °C for $Eu(hfc)_3$ and $Eu(tfc)_3$]) *in vacuo* for at least 3 h. Since it is difficult to obtain anhydrous $Pr(tta)_3$, $Pr(tfa)_3$, and $Eu(hfa)_3$ [5] the 1 : 2 hexamethylphosphoramide (HMP) adducts were used. The hydrated β-diketonates were prepared by the method of Belcher *et al.*[8] and the HMP adducts were obtained by dissolving the β-diketonate (1 equiv.) and HMP (3 equiv.) in carbon tetrachloride. Carbon tetrachloride and water were removed under reduced pressure and the $Eu(hfa)_3(HMP)_2$ and $Pr(tta)_3(HMP)_2$ adducts were recrystallized from carbon tetrachloride–light petroleum. $Eu(hfa)_3(HMP)_2$ (Found: C, 28·9; H, 3·6; F, 30·3; N, 7·5; P, 5·4. $C_{27}H_{39}EuF_{18}N_6O_8P_2$ requires C, 28·6; H, 3·4; F, 30·2; N, 7·4; P, 5·5%), $Pr(tta)_3(HMP)_2$ (Found: C, 37·4; H, 4·0; F, 14·6; N, 7·1; P, 5·4; S, 8·4. $C_{36}H_{48}F_9N_6O_8P_2PrS_3$ requires C, 37·2; H, 4·1; F, 14·7; N, 7·2; P, 5·3; S, 8·3%).

The $Pr(tfa)_3$–HMP adduct was used as an oil. The ratio of HMP to $Pr(tfa)_3$ was found by measuring the relative intensities of the co-ordinated HMP resonance and of the methyl resonance of $Pr(tfa)_3$.

Deuteriochloroform was stored over sodium hydrogen carbonate to remove any phosgene or hydrogen chloride, and carbon tetrachloride over sodium hydroxide pellets.[9] The solvents and substrates were dried over Linde 3A molecular sieves. The solutions were made up in a dry bag in the n.m.r. tube itself (previously heated and flushed with dry argon). The substrates were added using the normal syringe and rubber serum cap procedure. The volumes and hence the concentrations of the solutions were found by measuring the depths of liquid in precision bore n.m.r. tubes. Where necessary, the changes in concentration caused by cooling the solutions were estimated by measuring the depths of liquid at room temperature and at −78 °C in a solid CO_2–methanol bath. It can be assumed without serious error that the expansion is a linear function of the temperature over the range of temperatures studied.

The proton resonance spectra were obtained at 60 MHz on a Perkin-Elmer R12B spectrometer. The variable-temperature probe was calibrated before and after each kinetic experiment with a methanol sample using the calibration determined by van Geet.[10] At any setting on the dial the measured temperature remained constant to within 1 °C.

Line Shape Analysis.—Three life-times are of importance

---

* Ligand abbreviations are as follows. For compounds of the type $RCO{\cdot}CH{\cdot}COR'$:

	R	R′
fod-d_9	t-C_4D_9	C_3F_7
dpm	Bu^t	Bu^t
fhd	Me	C_3F_7
tta	CF_3	thenoyl
hfa	CF_3	CF_3
tfa	CF_3	Me

tfc = 3-(trifluoromethylhydroxymethylene)-(+)-camphorato
hfc = 3-(1,1,1,2,2,3,3-heptafluoropropylhydroxymethylene)-(+)-camphorato.

[1] For preliminary accounts see D. F. Evans and M. Wyatt, *J.C.S. Chem. Comm.*, 1972, 312; 1973, 339.

[2] J. K. M. Sanders and D. H. Williams, *Chem. Comm.*, 1970, 422.

[3] R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 1971, **93**, 1522.

[4] B. C. Mayo, *Quart. Rev.*, 1973, **2**, 49; R. Von Ammon and R. D. Fischer, *Angew. Chem. Internat. Edn.*, 1972, **11**, 675.

[5] J. Reuben, 'Progress in N.M.R. Spectroscopy,' Pergamon, 1972, vol. 9, part 1.

[6] F. A. Hart, J. E. Newberry, and D. Shaw, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3585; A. M. Grotens, J. J. M. Backus, E. de Boer, *Tetrahedron Letters*, 1973, 1467.

[7] C. S. Springer, D. W. Meek, and R. E. Sievers, *Inorg. Chem.*, 1967, **6**, 1105.

[8] R. Belcher, J. Majer, R. Perry, and W. I. Stephen, *J. Inorg. Nuclear Chem.*, 1969, **33**, 471.

[9] Naseer Ahmad, N. S. Bhacca, J. Selbin, and J. D. Wander *J. Amer. Chem. Soc.*, 1971, **93**, 2564.

[10] A. L. van Geet, *Analyt. Chem.*, 1970, **42**, 679.

in the present context, τ_f, the mean lifetime of the free substrate, τ_c, the mean lifetime of the complexed substrate, and τ, defined as $(\tau_c \cdot \tau_f)/(\tau_c + \tau_f)$.

Two techniques were used to obtain kinetic information from the observed spectra.

(1) *Complete line shape analysis.* This was applied to calculate τ in the region of intermediate exchange rates using the full expression given by Williams and Brown.[11]

A computer program calculated theoretical spectra for various values of τ and these spectra were then compared with those observed (see Figure 3). The program took account of $J(^{31}P-^{1}H)$ in HMP (9·4 Hz).

Values of δ in the coalescence region were obtained by interpolation of a graph of δ against T, using experimental measurements of δ obtained outside this region. Below the coalescence region, δ could be obtained directly. Above the coalescence region the shift of the single substrate resonance δ' relative to hexamethyldisiloxane or benzene was measured. The shift reagent–substrate complex is normally essentially undissociated (as indicated by the absence of any change in δ' on dilution) and the solvation number n is known. Hence δ is given by the expression

$$\delta = \frac{n + m}{n}(\delta' - \delta_B)$$

where m is the number of moles of free substrate per mole of shift reagent and δ_B is the separation between the reference and the free-substrate signals.

The half-width $\Delta^{\circ}_{\frac{1}{2}f}$ of the free substrate line in the absence of exchange was assumed to be the same as that of an inert reference (hexamethyldisiloxane or benzene). The half-widths of the reference signal were plotted against $1/T$.

$\Delta^{\circ}_{\frac{1}{2}c}$ Was obtained from the fast-exchange region using the expression

$$\Delta^{\circ}_{\frac{1}{2}c} = \frac{(n + m)\Delta'_{\frac{1}{2}} - m\Delta^{\circ}_{\frac{1}{2}f}}{n}$$

where $\Delta'_{\frac{1}{2}}$ = the half width of the substrate line in the fast-exchange region.

The calculated values of $\Delta^{\circ}_{\frac{1}{2}c}$ were plotted against $1/T$ and extrapolated to obtain $\Delta^{\circ}_{\frac{1}{2}c}$ in the coalescence region. In only one system [Yb(fod-d_9)$_3$–HMP in the mixed solvent] could the exchange processes be slowed down sufficiently for $\Delta^{\circ}_{\frac{1}{2}c}$ to be measured directly. Although the estimates of $\Delta^{\circ}_{\frac{1}{2}c}$ in the coalescence region are subject to appreciable error, it was found that the calculated spectra were insensitive to quite large changes in $\Delta^{\circ}_{\frac{1}{2}c}$. Any errors caused by partial decoupling of the ^{31}P–^{1}H coupling in systems involving HMP by the paramagnetic lanthanide ions [12] should be comparatively small. [In the Eu(hfa)$_3$–HMP system the ^{31}P–^{1}H splitting was observed for the co-ordinated HMP line at low temperatures.]

(2) *Line-width analysis.* This method was used to calculate values of τ_f in the slow-exchange region where two non-overlapping peaks are observed. Under these conditions $1/\tau_f = \pi(\Delta_{\frac{1}{2}f} - \Delta^{\circ}_{\frac{1}{2}f})$ where $\Delta_{\frac{1}{2}f}$ is the measured half-width of the substrate resonance.

A similar expression can be written for τ_c. However, no attempts were made to calculate τ_c, since the errors involved are now much more serious, and in most cases additional broadening from a second exchange process was observed.

For the HMP systems the observed resonances were compared with spectra calculated as the sum of two Lorentzian curves with appropriate half-widths and separated by $J(^{31}P-^{1}H)$ (9·4 Hz).

RESULTS AND DISCUSSION

Solvation Numbers.—For lanthanide shift reagent (R) and substrate (S) systems, two main equilibria (apart from solvent–substrate interactions) may be involved: *

$$\mathrm{R + S \rightleftharpoons RS} \qquad K_1 = \frac{[\mathrm{RS}]}{[\mathrm{R}][\mathrm{S}]} \qquad (1)$$

and

$$\mathrm{RS + S \rightleftharpoons RS_2} \qquad K_2 = \frac{[\mathrm{RS_2}]}{[\mathrm{RS}][\mathrm{S}]} \qquad (2)$$

In the early work on these systems only the first equilibrium was considered,[15] although Hinckley [16] in his pioneer work used a 1 : 2 reagent–substrate complex, namely Eu(dpm)$_3$(pyridine)$_2$. More detailed studies [13,17,18] have since shown the presence of the second equilibrium in a number of cases and have enabled approximate values for both K_1 and K_2 to be calculated.

If the chemical exchange between free and complexed substrate can be slowed down at low temperatures, then it is possible to determine directly and unambiguously the solvation number of the shift reagent, as was first done for the Eu(fod-d_9)$_3$–Me$_2$SO system in CD$_2$Cl$_2$.[1] This technique is restricted to systems containing strongly co-ordinating substrates for which K_1 will necessarily be large. The substrates studied were hexamethylphosphoramide (HMP), Me$_2$SO, tetramethylurea (TMU), and Et$_3$N and two solvents were used [C$_6$D$_5$CD$_3$ and CCl$_4$: CDCl$_3$: C$_6$D$_5$CD$_3$, 1·5 : 1·8 : 1 (v/v)]. Typical spectra are shown in Figures 1—3. At room temperature, a single substrate resonance is observed (two with Et$_3$N), but on cooling the solution this resonance broadens, and finally splits into two peaks, due to free and complexed substrate respectively. The solvation numbers given in Table 1 were normally calculated from the composition of the solutions and the relative areas of the free and complexed substrate peaks in the slow-exchange region. In a number of systems, on cooling below the coalescence region, the free substrate peak became progressively sharper, but the co-ordinated peak broadened extensively and in some cases, split (*e.g.* see Figure 4) presumably due to an intramolecular exchange process being slowed down. For a few systems showing this type of behaviour, it was

---

* There is evidence that certain lanthanide shift reagents can dimerize in solution;[13,14] also in one system the formation of RS$_3$ has been suggested.[13] However, in the present work there was no evidence for solvation numbers greater than 2.

[11] K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, 1966, **88**, 4134.

[12] S. S. Zumdahl and R. S. Drago, *Inorg. Chem.*, 1968, **7**, 2162.

[13] R. Porter, T. J. Marks, and D. F. Shriver, *J. Amer. Chem. Soc.*, 1973, **95**, 3548.

[14] R. G. Denning, F. J. C. Rossotti, and P. J. Sellars, *J.C.S. Chem. Comm.*, 1973, 381; D. Schwendiman and J. I. Zink, *Inorg. Chem.*, 1972, **11**, 3051 and references therein.

[15] *E.g.* I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Chem. Comm.*, 1971, 1281.

[16] C. C. Hinckley, *J. Amer. Chem. Soc.*, 1969, **91**, 5160.

[17] J. Reuben, *J. Amer. Chem. Soc.*, 1973, **95**, 3434.

[18] B. L. Shapiro and M. D. Johnston, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 8185.

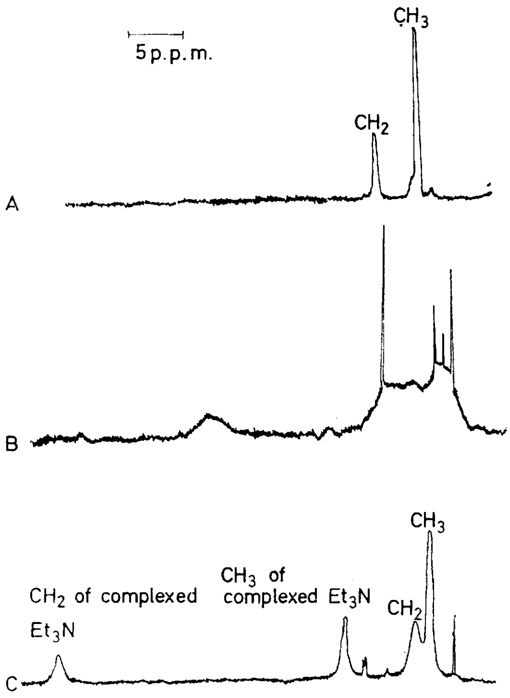

FIGURE 1 ^{1}H N.m.r. spectra of 0·218M-solution of Eu(fod-d_9)$_3$ and 0·441M-Et$_3$N in $C_6D_5CD_3$ at A, 80 °C; B, 0 °C; and C, −70 °C. The less intense resonances arise from the OCCHCO group, and the residual protium in the solvent and the C(CD$_3$)$_3$ group

impossible to make an accurate comparison of the intensities of the free and complexed substrate peaks. Accordingly, the solvation number was obtained by adding a known amount of an internal reference (hexamethyldisiloxane or benzene) and comparing the areas of the free substrate peak and that of the reference.

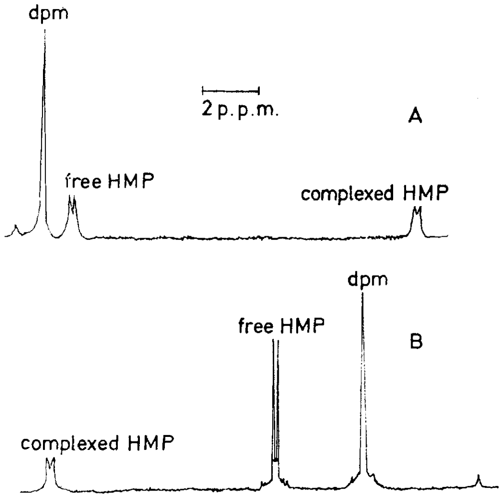

FIGURE 2 ^{1}H N.m.r. spectra of A, 0·0938M-solution of Pr(dpm)$_3$ and 0·178M-HMP in $C_6D_5CD_3$ at −60 °C; and B, 0·080M-solution of Eu(dpm)$_3$ and 0·181M-HMP at −80 °C in $C_6D_5CD_3$ at −80 °C

For most systems, as shown in Table 1, the solvation numbers (n) were either 1 or 2 to within experimental error (normally *ca.* 5%) corresponding to a low value of K_2 (<0·2) or a high value (>80 l mol^{-1}). However, in a number of cases fractional solvation numbers were observed. For both the Er(fod-d_9)$_3$–HMP and Yb(fod-d_9)$_3$–HMP systems, n was 1 ± 0·1 in the mixed solvent or in

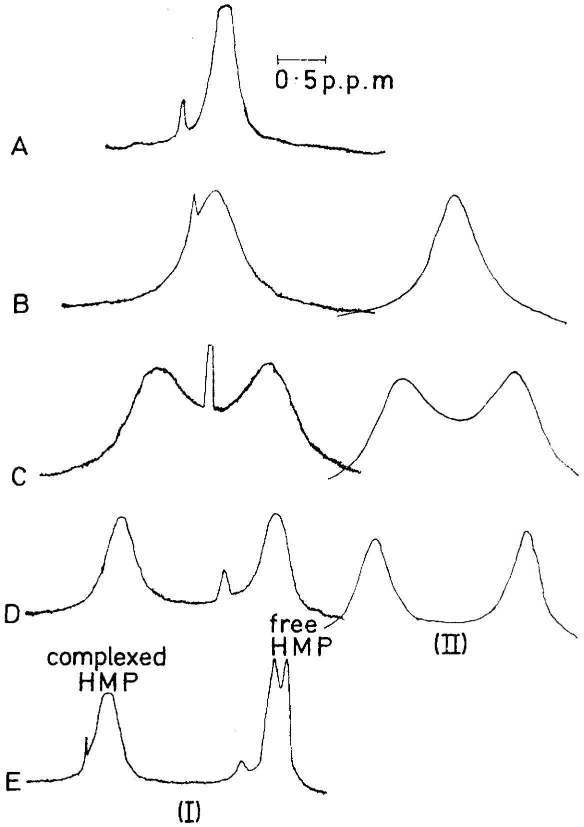

FIGURE 3 Observed (I) and calculated (II) ^{1}H n.m.r. spectra of 0·125M-solution of Eu(fod-d_9)$_3$ and 0·500M-HMP in the mixed solvent at A, 30 °C; B, 20 °C; C, 6 °C; D, −6 °C; and E, −16 °C

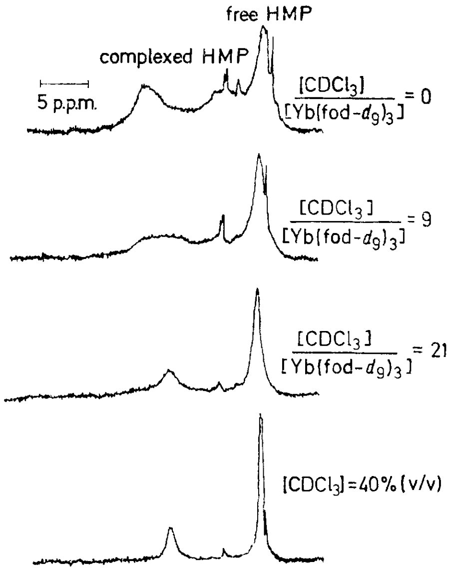

FIGURE 4 The effect of added $CDCl_3$ on the ^{1}H n.m.r. spectrum of 0·163M-solution of Yb(fod-d_9)$_3$ and 0·490M-HMP in $C_6D_5CD_3$ at −30 °C

$C_6D_5CD_3$–$CDCl_3$ mixtures containing more than *ca.* 40% (v/v) of $CDCl_3$, but in pure $C_6D_5CD_3$ at −30 °C a solvation number of 2 ± 0·1 was found. For $C_6D_5CD_3$–$CDCl_3$ mixtures with less $CDCl_3$ both 1 : 1 and 1 : 2 complexes could be detected (see Figure 4). This change in solvation number can be largely attributed to comparatively strong deuterium bonding between HMP and $CDCl_3$. (It is known that HMP forms stronger hydrogen bonds to $CHCl_3$ than does any other donor molecule tested.[19])

The two main equilibria are then

$$RS + S \rightleftharpoons RS_2 \qquad K_2' = \frac{[RS_2]}{[RS][S]} \qquad (3)$$

$$S + CDCl_3 \rightleftharpoons S,CDCl_3 \qquad K_3 = \frac{[S,CDCl_3]}{[S][CDCl_3]} \qquad (4)$$

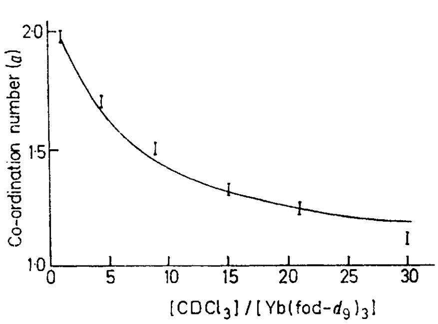

FIGURE 5 Observed (bars) and calculated solvation numbers in 0·163M-solution of Yb(fod-d_9)$_3$ and 0·490M-HMP at −30 °C (initial concentration in $C_6D_5CD_3$) as a function of the concentration of added $CDCl_3$

(*i.e.* both RS and $CDCl_3$ are competing for the substrate S). Since the co-ordination number is 2 ± 0·1 in $C_6D_5CD_3$ and 1 ± 0·1 in the mixed solvent both K_2' and K_3 must be large; *n* is then given by the expression

$$(1 - K_2'/K_3)n^2 + (c - m + mK_2'/K_3 + 2K_2'/K_3 - 1)n + (m - c - 2mK_2/K_3) = 0$$

where

$$[R]_{\text{initial}} = a$$
$$[S]_{\text{initial}} = ma$$
$$[CDCl_3]_{\text{initial}} = ac$$

This expression is valid when K_2' and K_3 are large and when

$$ac \geqslant ma - 2a$$
$$K_2 \text{ [in eqn. (2)]} = (n - 1)/a(2 - n)(m - n)$$

Figure 5 shows the experimental data for the Yb(fod-d_9)$_3$ system, and also the values of *n* calculated from the above expression with $K_2'/K_3 = 3$. The agreement is reasonably satisfactory especially in view of the experimental errors and the possibility that K_2' and K_3 may vary slightly as the solvent composition is changed. Fractional solvation numbers were also found with the following:

Shift reagent	Substrate	Solvent	K_2 (approx.)	T/K
Ho(fod-d_9)$_3$	HMP	Mixed	8	232
Eu(tfc)$_3$	HMP	$C_6D_5CD_3$	26	242
Eu(hfc)$_3$	HMP	$C_6D_5CD_3$	5	210

The solvation numbers in Table 1 were obtained at low temperatures and it is likely that the relative proportions of 1 : 1 complexes will increase in going to room temperature.

The following factors would seem to be important in determining the extent of formation of RS_2 complexes.

(1) The acceptor properties of the shift reagent. Ln(fod)$_3$ reagents are normally better acceptors than the corresponding Ln(dpm)$_3$ complexes,[3] presumably owing to the electronegative C_3F_7 group.

(2) The donor properties of the substrate. Of the four substrates studied, HMP is probably the best donor.[19]

(3) Solvation of the substrate as discussed above.

(4) In particular, steric repulsions in an actual or hypothetical eight-co-ordinate 1 : 2 complex. These steric repulsions will tend to increase with increasing size of the β-diketone and of the substrate (*in the vicinity of the co-ordinating site*), and with decreasing radius of the lanthanide ion. Non-bonded interactions between the substrate and the bulky shift reagent are not, of course, necessarily repulsive in nature. If the substrate is surrounded by atoms of the shift reagent at distances corresponding to the attractive part of the van der Waals potential, then stabilization of the adduct can result. This could be so in the 1 : 2 Ln(dpm)$_3$ adducts with pyridine and substituted pyridines, since *X*-ray studies show that in Ho(dpm)$_3$(4-picoline)$_2$ [20] and Eu(dpm)$_3$(pyridine)$_2$ [21] the substrate molecules have 11 close intermolecular contacts.[21] Further examples may be the surprisingly stable Pr(fod-d_9)$_3$,Et_3N and Eu(fod-d_9)$_3$,Et_3N adducts (Table 1 and Figure 1).

(5) It has been suggested by Reuben [17] that the relative values of K_1 and K_2 will depend on the substrate-induced ligand rearrangement around the lanthanide ion on forming RS which can either hinder or facilitate binding of the second substrate molecule.

The effect of some of the above factors can be illustrated with the following examples.

(a) *The size of the β-diketone ligand.* Whilst Pr(dpm)$_3$ and Eu(dpm)$_3$ give 1 : 1 adducts with HMP, Pr(fod-d_9)$_3$ and Eu(fod-d_9)$_3$ form 2 : 1 adducts under the same conditions. This can be largely attributed to the greater steric repulsions with the more bulky dpm reagents. In view of the very strong donor properties of HMP, the weaker acceptor properties of the dpm reagents are probably of secondary importance.

(b) *The radius of the lanthanide ion.* It is well known that the radii of the lanthanide ions decrease monotonically with increase in atomic number (lanthanide contraction). For the Ln(fod-d_9)$_3$–HMP systems in the mixed solvent the solvation numbers are 2 for Ln = Pr, Nd, Eu, and Tb, fractional for Ln = Ho and 1 for Ln = Er and Yb. This illustrates the increasing steric repulsions as the radius of the lanthanide ion decreases which

---

[19] H. Normant, *Angew. Chem. Internat. Edn.*, 1967, **6**, 1046.

[20] W. De W. Horrocks, jun., J. P. Sipe III, and J. R. Luber, *J. Amer. Chem. Soc.*, 1971, **93**, 5258.

[21] R. E. Cramer and K. Seff, *J.C.S. Chem. Comm.*, 1972, 400.

presumably outweighs any corresponding increase in acceptor properties. These two opposing factors are discussed more fully in the section on kinetics. Similar behaviour has been observed in Ln(fod)$_3$ systems at room temperature[13] where osmometric measurements show that the values of K_2 decrease steadily as the atomic number of the lanthanide increases.

(c) *The size of the substrate.* Although HMP is normally a better donor than Me$_2$SO, in the mixed solvent both Er(fod-d_9)$_3$ and Yb(fod-d_9)$_3$ form 1 : 2 adducts with Me$_2$SO, but 1 : 1 adducts only with HMP. This can be attributed to increased steric repulsions with the more bulky HMP molecule. It is noteworthy that Pr(fod-d_9)$_3$ and Eu(fod-d_9)$_3$ give 1 : 2 adducts with HMP, Me$_2$SO, and TMU but 1 : 1 adducts only with Et$_3$N. Although Et$_3$N is not a particularly bulky molecule, its steric requirements close to the N atom are quite large.

'Bound' Chemical Shifts.—Proton resonance spectra in the slow-exchange region also provide a direct measurement of the shift (s) induced in a substrate by co-ordination to the shift reagent (the 'bound' chemical shift δ). This information can also be obtained from room temperature spectra, but a full treatment[13,17,18] requires fitting of the data to an expression containing four unknowns K_1, K_2, δ_1, and δ_2, where δ_1 and δ_2 are the 'bound' chemical shifts for the 1 : 1 and 1 : 2 adducts respectively.

A complicating factor in considering the results in Table 1 is the variation of δ with temperature. Recently Bleaney[22] has shown theoretically that pseudo-contact shifts in complexes of the trivalent lanthanide ions (apart from Sm and Eu) should vary approximately as $1/T^2$. For europium complexes the expected temperature coefficient is much less. The experimental data of Grotens *et al.*[23] on the Pr(fod)$_3$ and Eu(fod)$_3$–dimethoxyethane (1 : 2) systems are in agreement with these predictions. In the present work detailed studies of the changes in δ with temperature were not attempted. (The range of temperature over which accurate measurements could be made was normally limited by both inter- and intramolecular exchange processes.) However, it was found that for europium shift reagents δ was only slightly dependent on the temperature. For praseodymium and neodymium shift reagents appreciable temperature coefficients were observed which varied from rather less than to rather greater than those expected theoretically, according to the particular system studied and also the temperature range. A possible complication with 1 : 2 adducts is the presence of two or more isomers in a labile and temperature dependent equilibrium. Also, any contact contribution to the observed value of δ will presumably have an approximate $1/T$ dependence. It can be seen from Table 1 that for a given substrate and lanthanide the values of δ are very dependent upon the nature of the β-diketone ligand, even when the differences in temperature are taken into account. This is consistent with previous room-temperature data.[4,5] One factor which may be involved is the differing stoicheiometry of the complexes. 1 : 2 Adducts might be expected to have generally smaller values of δ than 1 : 1 adducts as a result of partial averaging out due to the angular dependence of the induced shifts. [An extreme example is found in the Ln(H$_2$O)$_n^{3+}$ ions,* with $n = 8$ or 9 where the induced proton shifts are comparatively small.[24]] In the Yb(fod-d_9)$_3$–HMP system where both 1 : 1 and 1 : 2 adducts were characterized, the average shift for the 1 : 2 adduct (9·85 p.p.m.) is less than for the 1 : 1 adduct (10·90 p.p.m.) measured at the same temperature (243 K). This factor may partially account for the values of δ in Pr(dpm)$_3$,HMP and Eu(dpm)$_3$,HMP as compared with Pr(fod-d_9)$_3$,2HMP and Eu(fod-d_9)$_3$,2HMP. It has been noted by other workers that Ln(dpm)$_3$ shift reagents often induce larger limiting substrate shifts than do the corresponding Ln(fod)$_3$ reagents.[26] As a result of steric effects and the relative acceptor properties of the two types of reagent, 1 : 1 complexes should be more favoured with the Ln(dpm)$_3$ reagents.

For a given stoicheiometry, differences in the co-ordination polyhedron may be important, and also, as suggested by Horrocks and Sipe,[27] with a small β-diketone ligand a number of complexes with different geometries may coexist, which would tend to lead to small shifts. This would account for the small value of δ in the Eu(hfa)$_3$,2HMP adduct, although rather surprisingly the 'bound' chemical shift for Pr(tfa)$_3$,2HMP is greater than for both Pr(fod-d_9)$_3$,2HMP and Pr(tta)$_3$,2HMP.

The direct measurement of δ at low temperatures can have certain advantages. Reuben[17] has studied the Eu(fod)$_3$–Me$_2$SO system under conditions of rapid exchange at 30 °C in CCl$_4$. He estimates that $K_1 = 625$, $K_2 = 63{\cdot}4$ l mol^{-1}, and $\delta_1 = \delta_2 = 6{\cdot}58$ p.p.m. We find directly that $\delta_2 = 3{\cdot}42$ p.p.m. in CD$_2$Cl$_2$ at −80 °C[1] and 3·48 p.p.m. in C$_6$D$_5$CD$_3$ at −92 °C. In C$_6$D$_5$CD$_3$, δ_2 varies very little with temperature over the range −92 to −76 °C, and no reasonable extrapolation can give a value approaching Reuben's estimate, nor would such a marked solvent effect on δ_2 be expected.

A more likely explanation of Reuben's results is that his value for δ_1 is approximately correct, but that δ_2 is in fact very much lower. Also K_1 and K_2 are probably both very large so that the shape of his curve (Figure 5 in ref. 17) is largely determined by the ratio K_1/K_2.

Kinetics of Substrate Exchange.—The kinetics of substrate exchange were studied for most of the Ln(fod-d_9)$_3$

---

* When water is added to Pr(ClO$_4$)$_3$ in acetonitrile (0·84M) we find that δ (relative to the analogous Y^{3+} system) is −37·48 p.p.m. when [H$_2$O]/[Pr^{3+}] = 1 and −6·71 p.p.m. when [H$_2$O]/[Pr^{3+}] = 9. Similar results have been reported by Haas and Navon[25] in the Eu(ClO$_4$)$_3$–MeCN–H$_2$O system.

[22] B. Bleaney, *J. Magnetic Resonance*, 1972, **8**, 91.

[23] A. M. Grotens, J. J. M. Backus, and E. de Boer, *Tetrahedron Letters*, 1973, 1465.

[24] J. Reuben and D. Fiat, *Chem. Comm.*, 1967, 729.

[25] Y. Haas and G. Navon, *J. Phys. Chem.*, 1972, **76**, 1449.

[26] I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Chem. and Ind.*, 1972, 79; B. L. Shapiro, M. D. Johnston, jun., A. D. Godwin, T. W. Proulx, and M. J. Shapiro, *Tetrahedron Letters*, 1972, 3233.

[27] W. De W. Horrocks, jun., and J. P. Sipe III, *J. Amer. Chem. Soc.*, 1971, **93**, 6800.

systems given in Table 1. As described in the Experimental section, from line-shape analyses it is possible to derive reasonably accurate values for τ_f, the mean lifetime of the free substrate, and an average lifetime τ, equal to $\tau_f . \tau_c/(\tau_f + \tau_c)$. Reliable values of τ_c, the mean lifetime of the complexed substrate, could not normally be obtained directly.

The two most likely rate laws that would be expected for substrate exchange in an adduct RS_n are (i) $r = k_1[RS_n]$, first order, 'dissociative' mechanism and (ii) $r = k_2[RS_n][S]$, second order, 'associative' mechanism. For a first-order rate law, it can be shown that [28,29]

$$\frac{1}{\tau_f} = nk_1\frac{[RS_n]}{[S]}$$

$$\frac{1}{\tau_c} = k_1$$

and $$\frac{1}{\tau} = k_1\left(1 + n\frac{[RS_n]}{[S]}\right)$$

Similarly for second-order kinetics

$$\frac{1}{\tau_f} = nk_2[RS_n]$$

$$\frac{1}{\tau_c} = k_2[S]$$

and $$\frac{1}{\tau} = k_2(n[RS_n] + [S])$$

If both mechanisms contribute to the exchange process, then

$$\frac{1}{\tau_f} = nk_1\frac{[RS_n]}{[S]} + nk_2[RS_n], \quad etc.$$

The actual kinetics in any system can conveniently be found, either by varying the ratio $[RS_n]/[S]$ for a given substrate, or by keeping this ratio constant and varying the total concentration by diluting the original solution. Both methods were used but the second one was found to be the more convenient. It can be seen that for purely first-order kinetics τ_f and τ will be independent of concentration, and for purely second-order kinetics will vary as the inverse of concentration.

In all cases except two, the kinetics of substrate exchange were found to be entirely first order (RS_2 adducts) or entirely second order (RS adducts) within experimental error. Since $k_{1(2)} = \frac{kT}{h} e^{-\Delta H^{\ddagger}/RT} . e^{\Delta S^{\ddagger}/R}$ a least-squares plot of log $k_{1(2)}/T$ against $1/T$ enables $\Delta H^{\circ\ddagger}$, the enthalpy of activation, and $\Delta S^{\circ\ddagger}$, the entropy of activation, to be obtained.

For the adducts $Pr(fod\text{-}d_9)_3,2Me_2SO$ and $Nd(fod\text{-}d_9)_3,$-$2Me_2SO$ in the mixed solvent both first- and second-order mechanisms were significant. In these systems, values of τ were calculated at a series of temperatures for three solutions of differing total concentration but with $[RS_2]/[S]$ constant (0·5). We then have

$$\frac{1}{\tau} = \frac{kT}{h}\left[\left(1 + \frac{2[RS_2]}{[S]}\right)e^{-\Delta H_1^{\ddagger}/RT} . e^{-\Delta S_2^{\ddagger}/R} + (2[RS_2] + [S])e^{-\Delta H_2^{\ddagger}/RT} . e^{-\Delta S^{\ddagger}/R}\right]$$

A computer program varied $\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$, $\Delta H_2^{\ddagger}$, and $\Delta S_2^{\ddagger}$ to give the best fit to the observed values of τ. This procedure was necessary since the second-order mechanism made a significant contribution over a limited temperature range only. For this reason, the values of $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ are less accurate than those for $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$.

The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ and also of k_1 and k_2 at a single temperature are collected in Table 2. If we consider the first-order exchange processes it can be seen that with all three substrates the kinetics show a very marked variation in going from Ln = Pr to Ln = Yb. Regardless of the intimate mechanism of exchange it might be expected that both $\Delta H^{\ddagger}$ and k_1 could be related to the relative stability of the bis-adducts. As indicated in the section on solvation numbers, as the atomic number of the lanthanide increases, and its ionic radius concomitantly decreases, there will be two opposing effects. First, in the absence of steric factors the acceptor properties of the shift reagent will presumably increase. Secondly, steric repulsions in the RS_2 adducts will also increase, which will tend to make these adducts less stable. The interplay of these two effects is well illustrated in Figure 6, which shows a plot of log k_1 against the eight-co-ordinate ionic radius of the lanthanide ion.[30] k_1 Is considered rather than $\Delta H^{\ddagger}$, since it provides a much more sensitive parameter and also the available data are more extensive. The curves in Figure 6 can readily be interpreted in terms of the relative sizes of the substrate molecules. With the smallest substrate, Me_2SO, the values of k_1 decrease from Pr to Eu, and then increase rapidly from Eu to Yb. For the TMU systems, k_1 is very similar for the Pr and Eu adducts, and then increases in a similar manner. HMP is the bulkiest substrate and here the steric factor is predominant since k_1 increases monotonically as the atomic number of the lanthanide increases. In spite of these steric effects the values of $\Delta H^{\circ\ddagger}$ are considerably greater than those for the Me_2SO and TMU adducts, which reflects the very strong donor properties of the HMP molecule.

For the bis-adducts, second-order exchange processes were significant only with $Pr(fod\text{-}d_9)_3,2Me_2SO$ and $Nd(fod\text{-}d_9)_3,2Me_2SO$. The comparatively small size of the Me_2SO molecule and the large ionic radius of the Pr^{3+} and Nd^{3+} ions will favour an associative mechanism involving RS_3 intermediates.

It has been noted previously that both RS and RS_2

---

[28] A. Loewenstein and T. M. Connor, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 280.

[29] D. R. Eaton and K. Zaw, *Canad. J. Chem.*, 1971, **93**, 3281.

[30] R. D. Shannon and C. T. Previtt, *Acta Cryst.*, 1969, **B25**, 925.

TABLE 1

Solvation numbers and ' bound ' chemical shifts for lanthanide shift reagent systems

Shift reagent [a]	Substrate	Solvent	Solvation number	Shift δ (p.p.m.)	Temp. (t/°C)
Pr(fod-d_9)$_3$	HMP	Mixed	2	+2·71 [b]	−40
Pr(fod-d_9)$_3$	HMP	$C_6D_5CD_3$	2	+2·40 [b]	−20
Pr(fod-d_9)$_3$	Me_2SO	Mixed	2	+25·2	−92
Pr(fod-d_9)$_3$	TMU	$C_6D_5CD_3$	2	+1·9	−66
Pr(fod-d_9)$_3$	Et_3N	$C_6D_5CD_3$	1	CH_2, +46·6; CH_3, +17·9	−60
Nd(fod-d_9)$_3$	HMP	$C_6D_5CD_3$	2	+2·85 [b]	−30
Nd(fod-d_9)$_3$	Me_2SO	Mixed	2	+6·75	−92
Nd(fod-d_9)$_3$	HMP	Mixed	2	+3·24 [b]	−60
Eu(fod-d_9)$_3$	HMP	$C_6D_5CD_3$	2	−2·29 [b]	−20
Eu(fod-d_9)$_3$	HMP	Mixed	2	−2·71 [b]	−42
Eu(fod-d_9)$_3$	Me_2SO	Mixed	2	−3·48	−92
Eu(fod-d_9)$_3$	TMU	$C_6D_5CD_3$	2	−1·39	−66
Eu(fod-d_9)$_3$	Et_3N	$C_6D_5CD_3$	1	CH_2 −30·5/CH_3 −7·5	−60
Tb(fod-d_9)$_3$	HMP	$C_6D_5CD_3$	2	+33·0 [b]	+16
Tb(fod-d_9)$_3$	HMP	Mixed	2	+32·5 [b]	+16
Tb(fod-d_9)$_3$)	Me_2SO	Mixed	2	— [c]	−90
Ho(fod-d_9)$_3$	HMP	Mixed	Fractional	— [c]	−40
Ho(fod-d_9)$_3$	HMP	$C_6D_5CD_3$	2	+11·8/33·6 [b]	−40
Ho(fod-d_9)$_3$	Me_2SO	$C_6D_5CD_3$	2	— [c]	−90
Er(fod-d_9)$_3$	HMP	$C_6D_5CD_3$	2	— [c]	−40
Er(fod-d_9)$_3$	HMP	Mixed	1	−9·4	−40
Er(fod-d_9)$_3$	TMU	$C_6D_5CD_3$	2	— [c]	−90
Er(fod-d_9)$_3$	Me_2SO	Mixed	2	— [c]	−90
Yb(fod-d_9)$_3$	HMP	$C_6D_5CD_3$	2	+4·25/14·3 [b]	−30
Yb(fod-d_9)$_3$	HMP	Mixed	1	−11·33	−40
Yb(fod-d_9)$_3$	Me_2SO	Mixed	2	— [c]	−90
Yb(fod-d_9)$_3$	TMU	$C_6D_5CD_3$	2	— [c]	−90
Pr(dpm)$_3$	HMP	Mixed	1	+12·71	−60
Eu(dpm)$_3$	HMP	Mixed	1	−7·64	−60
Pr(fhd)	HMP	Mixed	2	— [b]	−80
Eu(fhd)$_3$	HMP	Mixed	2	−2·80 [b]	−76
Pr(tta)$_3$	HMP	Mixed	2	+2·26	−80
Eu(hfa)$_3$	HMP	Mixed	2	0·87	−30
Pr(tfa)$_3$	HMP	$C_6D_5CD_3$	2	+5·02	−60
Eu(tfc)$_3$	HMP	$C_6D_5CD_3$	Fractional		−60
Eu(hfc)$_3$	HMP	$C_6D_5CD_3$	Fractional		−30

[a] See footnote on p. 765 for ligand abbreviations. [b] At low temperatures, the complexed HMP peak broadens and splits, presumably due to an intramolecular exchange process being slowed down. [c] Solvation numbers obtained by measuring the relative intensities of the free substrate and a known amount of an inert reference.

TABLE 2

Kinetic data for Ln(fod-d_9)$_3$S$_2$ complexes

Ln	Substrate	Solvent	Mechanism (order)	$\Delta H_1^‡$ [a]	$\Delta S_1^‡$ [b]	k_1 [c]	T_1/K	$\Delta H_2^‡$ [a]	$\Delta S_2^‡$ [b]	k_2 [d]	T_2/K
Pr	Me_2SO	Mixed	1st + 2nd	37·6	3	143	186·2	27·6	−39	612	186·2
Nd	Me_2SO	Mixed	1st + 2nd	38·1	0	84·9	186·2	24·7	−60	328	186·2
Eu	Me_2SO	Mixed	1st	39·7	0	29·7	186·2				
Tb	Me_2SO	Mixed	1st			131	186·2				
Ho	Me_2SO	Mixed	1st			223	186·2				
Er	Me_2SO	Mixed	1st			245	186·2				
Yb	Me_2SO	Mixed	1st			549	186·2				
Pr	TMU	$C_6D_5CD_3$	1st	41·5	−3	6·4	186·2				
Eu	TMU	$C_6D_5CD_3$	1st	41·9	−2	4·1	186·2				
Er	TMU	$C_6D_5CD_3$	1st			141	186·2				
Yb	TMU	$C_6D_5CD_3$	1st			247	186·2				
Pr	HMP	$C_6D_5CD_3$	1st	55·1	−12	38·0	273·2				
Eu	HMP	$C_6D_5CD_3$	1st	54·6	−10	65·9	273·2				
Tb	HMP	$C_6D_5CD_3$	1st	54·2	−3	167	273·2				
Ho	HMP	$C_6D_5CD_3$	1st	50·3	−10	426	273·2				
Er	HMP	$C_6D_5CD_3$	1st	52·5	2	702	273·2				
Yb	HMP	$C_6D_5CD_3$	1st	50·5	3	2570	273·2				
Eu	HMP	Mixed	1st	53·0	−13	91·9	273·2				
Tb	HMP	Mixed	1st			180	273·2				
Er	HMP [e]	Mixed	2nd					25·8	−80	419	273·2
Yb	HMP [e]	Mixed	2nd					24·6	−87	349	273·2
Eu	Et_3N [e]	$C_6D_5CD_3$	1st + 2nd			*ca.* 160 [f]	243			*ca.* 460 [f]	243
Pr	EtN [e]	$C_6D_5CD_3$	1st + 2nd			*ca.* 330 [f]	203			*ca.* 320 [f]	203

[a] $\Delta H_1^‡$ and $\Delta H_2^‡$ in kJ mol^{-1}. [b] $\Delta S_1^‡$ and $\Delta S_2^‡$ in J K^{-1} mol^{-1}. [c] k_1 In s^{-1} at temperature T_1. [d] k_2 in mol l^{-1} s^{-1} at temperature T_2. [e] These adducts were Ln(fod-d_9)S. [f] Calculated from line-widths of *co-ordinated* CH_2 resonances, treated as overlapping 1.3.3.1 Lorentzians.

species could be detected in the proton resonance spectra of the Er- and Yb-(fod-d_9)$_3$–HMP systems in certain $C_6D_5CD_3$–$CDCl_3$ mixtures. The free HMP resonances were quite sharp (Figure 4). This implies that there is a considerable potential energy barrier for the reactions

$$\text{(Er or Yb)(fod-}d_9)_3\text{HMP} + \text{HMP} \rightleftharpoons \text{(Er or Yb)(fod-}d_9)_3\text{(HMP)}_2$$

since otherwise rapid intermolecular exchange would be expected. This potential energy barrier is presumably due to a high rearrangement energy in going from a seven-co-ordinate structure to an eight-co-ordinate one, especially with the bulky HMP substrate. A tentative reaction profile for first-order exchange in RS_2 adducts or second-order exchange in RS adducts is shown in Figure 7. RS_2* is regarded as an unstable isomer of RS_2 in which the configuration of the β-diketone ligands is similar to that in the seven-co-ordinate RS. This reaction profile is consistent with the following observed features (see Table 2).

(1) The small values of $\Delta S_1^‡$ and the large and negative values of $\Delta S_2^‡$. (2) For both the Er- and Yb-(fod-d_9)$_3$–HMP systems $\Delta H_1^‡$ is much greater than $\Delta H_2^‡$. (3) For Eu(fod-d_9)$_3$,2HMP, $\Delta H_1^‡$ and k_1 at 273 K are only slightly affected when the solvent is changed from $C_6D_5CD_3$ to the mixed solvent.

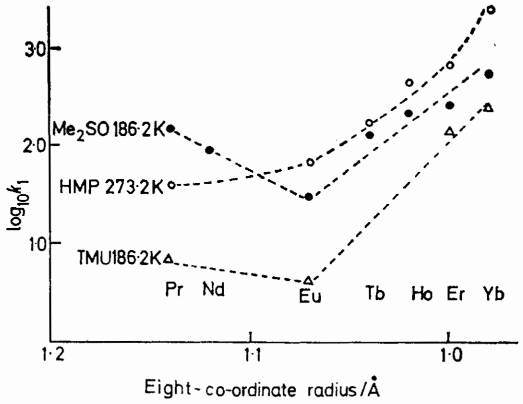

FIGURE 6 Plot of $\log_{10}k_1$ against the eight-co-ordinate ionic radius [30] of the lanthanide ion for Ln(fod-d_9) complexes

Quantitative kinetic data were obtained only with the systems given in Table 2. However, it is possible to derive qualitative kinetic information for a number of the other systems studied including those in which it was not possible to slow down the substrate exchange (at the coalescence temperature for equal populations of the two sites $\tau = 2^{\frac{1}{2}}\pi/\delta$).[31] Thus, for the Eu(fod-d_9)$_3$–Et_3N system in $C_6D_5CD_3$ where only RS species are present (see Table 1) substrate exchange was effectively slowed down at a relatively high temperature (*ca.* −40 °C). In the corresponding n-propylamine system, exchange was fast even at −100 °C. It seems unlikely that this difference can be explained in terms of the relative donor abilities of the two substrates. More probably, because of its smaller steric requirements propylamine can form 1 : 2 adducts, which then undergo relatively rapid substrate exchange by a first-order mechanism. Similarly, in contrast to the corresponding fod-d_9 system, substrate exchange was not slowed down at −100 °C for the Eu(dpm)$_3$–Me_2SO system in the mixed solvent. This can be attributed to relative instabilities of the 1 : 1 and/or 1 : 2 adducts, as a consequence of steric effects, and the weaker acceptor properties of the dpm shift reagents. However, this behaviour may not be typical of all dpm and fod systems; possibly as a result of specific van der Waals interactions of the type described in the section on solvation numbers. Cramer and Dubois [32] have apparently demonstrated that substrate exchange is slow for the Eu(dpm)$_3$,2β-picoline adduct in CS_2 at −115 °C. In the Eu(fod-d_9)$_3$–γ-picoline system at −96 °C ($C_6D_5CD_3$) we find that the substrate resonances are only beginning to broaden due to partial slowing down of the intermolecular exchange.

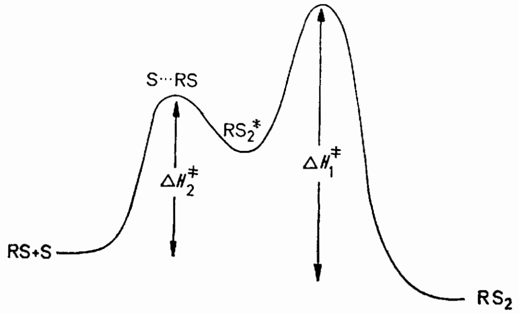

FIGURE 7 Suggested energy profile for substrate exchange

We thank the S.R.C. for a postgraduate studentship (to M. W.).

[3/1739 *Received*, 16th *August*, 1973]

---

[31] J. A. Pople, W. G. Schneider, and M. J. Bernstein, 'High-resolution Nuclear Magnetic Resonance,' McGraw–Hill, 1959.

[32] R. E. Cramer and R. Dubois, *J. Amer. Chem. Soc.*, 1973, **95**, 3801.