Calorimetric Titration Studies of Adduct Formation between Lanthanide β-Diketonates and Organic Bases in Benzene Solution

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The technique of titration calorimetry has been used to study the reactions of lanthanide shift reagents with organic substrates in benzene solution. Stability constants and enthalpies and entropies of formation have been determined for adducts of tris(2,2,6,6-tetramethylheptane-3,5-dionato)-europium(III) and -ytterbium(III) and tris(6,6,7,7,-8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)-europium(III) and -praseodymium(III) with pyridine, 2-methyl-, 3-methyl-, and 4-methyl-pyridine, 2,4,6-trimethylpyridine, dimethyl sulphoxide, and pyridine *N*-oxide. Adduct-formation constants mostly lie in the range $2 < \log K < 4$ and enthalpies of adduct formation in the range $15 < -\Delta H^{\ominus} < 35$ kJ mol^{-1} with some variations which can be related to steric effects. Unusual positive entropy changes associated with the formation of adducts of the fluorinated reagents can be correlated with their unusually high solubility.

LANTHANIDE β-diketonate complexes have been widely used as shift reagents to obtain improved resolution of n.m.r. spectra. Their effectiveness depends upon the formation of addition compounds with the organic substrate in which the effective magnetic field at each hydrogen atom in the substrate is modified by the proximity of the paramagnetic metal atom. Crystallographic studies of many of these compounds have shown that the co-ordination number of the lanthanide atom in the addition compounds is increased to seven, eight, or even nine. Thus, seven-co-ordination is observed in [Eu(tmhd)$_3$(dmso)] (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate, dmso = dimethyl sulphoxide),[1] [Ho(dppd)$_3$(OH$_2$)] (dppd = 1,3-diphenylpropane-1,3-dionate),[2] and [Yb(acac)$_3$(OH$_2$)] (acac = pentane-2,4-dionate) [3] and eight-co-ordination in [Eu(acac)$_3$(phen)] (phen = 1,10-phenanthroline),[4] [Eu(tmhd)$_3$(py)$_2$] (py = pyridine),[5] [Eu(tmhd)$_3$(dmf)$_2$] (dmf = *NN*-dimethylformamide),[1] [Eu(tmhd)$_3$(phen)],[1] and [Ho(tmhd)$_3$(4Me-py)$_2$] (4Me-py = 4-methylpyridine) [6] and nine-co-ordination in [(tfacm)$_3$Pr(dmf)$_3$Pr(tfacm)$_3$] (Htfacm = 3-trifluoroacetyl-D-camphor).[7] Seven-co-ordination is also achieved in the dimeric complex [Pr$_2$(tmhd)$_6$] [8] by sharing of co-ordinated oxygen atoms.

Adduct formation is usually incomplete in solution and, since equilibrium is reached rapidly on the n.m.r. time scale, the observed n.m.r. spectra are averages of those of the free and complexed substrates and are affected by the concentration and by adduct-formation constants. The improved performance of fluorinated shift reagents is at least partly due to their increased Lewis acidity, leading to more stable addition compounds with the organic substrates.[9]

Attempts to obtain adduct-formation constants from n.m.r. data have not proved very successful and it has sometimes not even been possible to determine satisfactorily the reaction stoicheiometry.[10] Better results have been obtained by fluorescence spectroscopy, but this technique is restricted by the failure of some systems to give suitable spectra, although it does reveal the importance of eliminating the last traces of water from these systems.[11]

In the present paper we report the application of the technique of calorimetric titration to the determination of adduct-formation constants for several systems; this technique has also made possible for the first time the determination of enthalpy changes for the reactions.

EXPERIMENTAL

Materials.—The shift reagents, [Eu(tmhd)$_3$], [Eu(fod)$_3$] (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate), [Pr(tmhd)$_3$], [Pr(fod)$_3$], and [Yb(tmhd)$_3$], were Aldrich 'Resolve-Al 99+% gold label' chemicals and were used without further purification. Heterocyclic bases, gas-chromatographic quality, from Tokyo Kasei, Japan, were redistilled and dried over anhydrous potassium carbonate. Dimethyl sulphoxide (B.D.H.) was dried over anhydrous calcium sulphate, then distilled through a fractionating column and the middle fraction stored over a 4A molecular sieve in a desiccator. Pyridine *N*-oxide (B.D.H.) was purified by sublimation *in vacuo* and stored over silica gel in a desiccator. 'Crystallisable, sulphur-free' benzene (May and Baker) was purified by freezing, discarding the first 5% to melt, distilling the remainder through a fractionating column, and storing over calcium hydride.

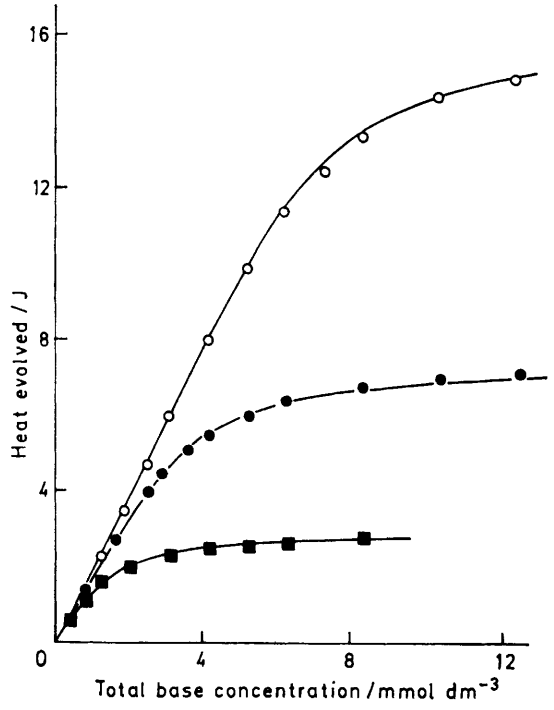
Molecular Weights.—Molecular weights of shift reagents were determined cryoscopically in benzene in an apparatus specially constructed so that traces of water could be removed by azeotropic distillation of part of the solvent in an atmosphere of dry nitrogen, the distillate being collected on phosphorus pentaoxide before making measurements.

Calorimetry.—Benzene solutions of the shift reagents in the concentration range 10^{-4}—10^{-2} mol dm^{-3} were prepared by weighing the appropriate amount of reagent and dissolving it in pure toluene (*ca.* 10 cm^3); traces of water were then removed azeotropically by distillation of the toluene on to P_2O_5 in an atmosphere of dry nitrogen, until the residual volume was less than 1 cm^3; the volume was then made up to 100 cm^3 with dry benzene. The entire preparation of the solution was carried out in a specially constructed apparatus, without allowing exposure to air. The solution was then transferred to the calorimeter under dry nitrogen and titrated with a solution of the base in dry benzene of a concentration about 100 times that of the solution of shift reagent.

All calorimetric titrations were carried out in a LKB 8 700 calorimeter, using the previously described tech-

nique; [12] all measurements were made at 30.0 °C. Briefly, solutions of base were added in small increments and the heat evolved was measured after each addition. Control titrations were made into pure solvent to enable corrections to be made for the heat of dilution of the base. Thermograms were obtained by plotting the cumulative heat of reaction, after correcting for dilution effects, against the total base concentration. In each titration, heat changes were measured by reference to two internal electrical calibrations.

Reaction stoicheiometries were obtained from the thermograms by trial fitting of the experimental data to computed curves. For systems of 1 : 1 stoicheiometry, the approximate overall enthalpy change was obtained by extrapolation of the cumulative, corrected, heat of reaction and equilibrium constants calculated at each experimental point on the thermogram; the enthalpy change was then refined iteratively until constant values of the adduct-formation constant, K, were obtained throughout the titration. For each system, data were obtained at at least three different concentrations of the shift reagent. In the tables of results, uncertainties in K are the sum of the average standard deviation of K in individual titrations and the mean deviation of K in different titrations; uncertainties in ΔH are



Calorimetric titration of 4-methylpyridine into $[Eu(fod)_3]$ in benzene at 30 °C. Experimental points for $[Eu(fod)_3]$: concentration = 3.19 (○), 1.58 (●), and 0.53 (■) mmol dm^{-3}. Curves computed for $K_1 = 2 \times 10^4$, $K_2 = 1 \times 10^3$ dm^3 mol^{-1}; $\Delta H_1^{\ominus} = -18$, $\Delta H_2^{\ominus} = -33$ (○); $\Delta H_1^{\ominus} = -17$, $\Delta H_2^{\ominus} = -30$ (●); $\Delta H_1^{\ominus} = -19$, $\Delta H_2^{\ominus} = -36$ (■) kJ mol^{-1}

mean deviations from the average of values obtained in different titrations. Uncertainties in ΔG and ΔS are derived.

Systems involving two successive equilibria were analysed in terms of four parameters K_1, K_2, ΔH_1, and ΔH_2. Approximate values of K_1 and K_2 were first obtained by the extrapolation technique previously described [13] and ΔH_1 and ΔH_2 then obtained to give the best fit of computed thermograms to the experimental points. For each individual titration this process was repeated using new values of K_1 and K_2, selected at intervals of 0.15 in log K. When the best set of parameters had been obtained for each individual titration, the mean values of K_1 and K_2 were selected and the best-fit values of ΔH_1 and ΔH_2 obtained for each titration using these mean values of K_1 and K_2. It was found to be impossible to improve the fit of computed thermograms to experimental points by taking values of K_1 or K_2 at intervals less than 0.15 in log K and values of log K_1 and log K_2 are given uncertainties of ± 0.3 in the tables of results. Uncertainties in ΔH_1 and ΔH_2 are mean deviations from the average of the values obtained in individual titrations. The Figure shows a typical example of the fit of computed curves to experimental points.

RESULTS AND DISCUSSION

$[Yb(tmhd)_3]$.—Data obtained for the reaction of this shift reagent with three heterocyclic bases in benzene solution gave excellent fits for 1 : 1 stoicheiometry, equation (1), and cryoscopic measurements of the molecular weight

$$[Yb(tmhd)_3] + \text{base} \rightleftharpoons [Yb(tmhd)_3(\text{base})] \quad (1)$$

gave a value of m.w./f.w. = 1.03 (f.w. = formula weight) at a concentration of 3.8×10^{-2} mol dm^{-3}. Although the crystal structure of the compound $[Yb(tmhd)_3]$ has not been reported, it is isostructural with $[Er(tmhd)_3]$ and $[Lu(tmhd)_3]$, both of which have been shown to be monomeric and six-co-ordinate in the solid state.[14,15]

Thermodynamic data for the formation of adducts of $[Yb(tmhd)_3]$ with pyridine, 4-methylpyridine, and 2-methylpyridine 2Me-py are shown in Table 1. The enthalpy changes of *ca.* −20 kJ mol^{-1} are comparable to those previously observed for the addition of pyridine to β-diketone complexes of copper(II),[12] nickel(II),[16] or zinc(II).[17] The stabilities of the adducts with $[Yb(tmhd)_3]$ are, however, a little higher and the entropy changes accompanying adduct formation are very small. Nevertheless, as in the other systems, adduct formation is entropy resisted and substitution of a methyl group adjacent to the donor atom in pyridine leads to much lower adduct stability and a slightly less negative enthalpy of adduct formation; these changes can be attributed to direct steric interference between this methyl group and the β-diketone rings in the adduct.

$[Eu(tmhd)_3]$.—Experimental calorimetric titration data could only be fitted satisfactorily to computed thermograms by assuming a stoicheiometry in which dimeric $[Eu_2(tmhd)_6]$ reacted with base without disruption, according to equation (2). Association of the shift

$$[Eu_2(tmhd)_6] + \text{base} \rightleftharpoons [Eu_2(tmhd)_6(\text{base})] \quad (2)$$

reagent in benzene solution was confirmed cryoscopically, values of m.w./f.w. ranging from 1.6 in 6×10^{-3} mol dm^{-3} solution to 1.9 in 2×10^{-2} mol dm^{-3}. This compound has previously been reported as monomeric in hexane solution; [18] the technique then used was osmometry, which depends upon the rate of vapourisation of solvent from a small drop of solution into a relatively

large vapour space and is consequently most likely to be sensitive to trace amounts of moisture; it is thus possible that the results could refer to a seven-co-ordinate water adduct and it can be shown that a partial water vapour pressure of 10^{-4} Torr * in a 1-l vapour space provides enough water to convert into the water adduct all of the shift reagent in a droplet of 1-mm diameter. The corresponding praseodymium compound has been shown to be dimeric, $[Pr_2(tmhd)_6]$, in the solid state and all the compounds from $[La(tmhd)_3]$ to $[Dy(tmhd)_3]$ are isostructural; [8] furthermore, among nearly 40 β-diketonate derivatives of the elements from La to Dy, whose structures have been determined, there is not one with a co-ordination number less than seven. It thus seems that spontaneous dissociation of the dimeric species into monomers in solution in non-donor solvents is unlikely and the values of m.w./f.w. less than 2.0 observed by us and others probably arise from the extreme difficulty of totally excluding water from these systems. Our calorimetric data gave no evidence for the formation of monomeric species, either anhydrous or hydrated, and gave excellent fits of experimental points to computed thermograms when treated as 1 : 1 reactions according to equation (2).

TABLE 1

Thermodynamic data for the reaction $[Yb(tmhd)_3]$ + base ⇌ $[Yb(tmhd)_3(base)]$ in benzene solution at 30 °C

Base	[Yb]/ mmol dm^{-3}	log(K/ dm^3 mol^{-1})	$-\Delta H^\ominus$/ kJ mol^{-1}	$-\Delta G^\ominus$/ kJ mol^{-1}	$\Delta S^\ominus$/ J K^{-1} mol^{-1}
Pyridine	1.3—2.8	3.14 ± 0.05	22.7 ± 1.1	18.2 ± 0.3	−15 ± 5
4Me-py	1.5—7.3	3.27 ± 0.07	22.8 ± 2.6	18.9 ± 0.4	−13 ± 10
2Me-py	1.9—8.9	2.16 ± 0.06	18.0 ± 1.2	12.5 ± 0.4	−18 ± 5

$[Eu(fod)_3]$.—No crystal structure has yet been reported for an adduct-free compound of the fod series. Structural studies have shown that in a series of adducts of tris-[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato]neodymium $[Nd(tftbd)_3]$ the metal is eight-co-ordinate,[19] as it is in $[Eu(tftbd)_3(OH_2)_2]$.[20] The only reported structures of fod complexes are both seven-co-ordinate: $[Lu(fod)_3(OH_2)]$ [21] and a curious hydrated dimer of $[Pr(fod)_3]$,[22] in which an oxygen-bridged structure occurs like that in $[Pr_2(tmhd)_6]$. The structure of this hydrated dimer lends support to our conclusion above that an analogous adduct is formed in solution when bases add to $[Eu_2(tmhd)_6]$. The increased volatility and greatly increased solubility of the fod complexes suggests that they are monomeric in solution, although association of $[Pr(fod)_3]$ and $[Eu(fod)_3]$ has been shown to occur at concentrations above 0.02 mol dm^{-3}.[23] Cryoscopic measurements in benzene gave values of m.w./f.w. of 0.88—1.13 for $[Eu(fod)_3]$ in the concentration range 1.1×10^{-2}—3.0×10^{-2} mol dm^{-3}.

TABLE 2

Thermodynamic data for the reaction $[Eu_2(tmhd)_6]$ + base ⇌ $[Eu_2(tmhd)_6(base)]$ in benzene solution at 30 °C

Base	[Eu_2]/ mmol dm^{-3}	log(K/ dm^3 mol^{-1})	$-\Delta H^\ominus$/ kJ mol^{-1}	$-\Delta G^\ominus$/ kJ mol^{-1}	$\Delta S^\ominus$/ J K^{-1} mol^{-1}
Pyridine	1.6—5.1	3.59 ± 0.07	33.2 ± 1.8	20.8 ± 0.4	−41 ± 7
4Me-py	2.3—6.1	3.34 ± 0.20	29.8 ± 3.8	19.3 ± 1.1	−35 ± 16
3Me-py	2.1—5.7	3.17 ± 0.07	35.6 ± 2.6	18.4 ± 0.4	−57 ± 10
2Me-py	2.8—8.5	2.35 ± 0.06	21.6 ± 2.6	13.6 ± 0.3	−26 ± 10
dmso	2.1—3.9	4.53 ± 0.02	35.6 ± 2.4	26.3 ± 0.2	−31 ± 8
pyo	1.8—6.8	>5	26.0 ± 3.6	>29	<−10

Thermodynamic data for the formation of the adducts $[Eu_2(tmhd)_6(base)]$ with four heterocyclic bases and the oxygen donors dimethyl sulphoxide and pyridine *N*-oxide (pyo) are shown in Table 2. Enthalpy changes are all negative and comparable in magnitude to those observed in base-adduct formation by other metal β-diketone complexes (see above), but the adduct stability constants are rather higher than usual; as in other similar systems, adduct formation is entropy resisted, reflecting the formal decrease in the total number of particles in solution.

When the base added is pyridine *N*-oxide there is a small positive entropy change, which leads to an unexpectedly high adduct stability. This probably arises from the low steric interaction between the metal complex and the oxygen donor, which is attached to only one other atom. A similar effect could be expected with dimethyl sulphoxide and is also observed, but is less pronounced, leading to higher adduct stability, although the entropy change remains negative; this too can be explained on steric grounds since the two CH_3 groups in dimethyl sulphoxide would provide a greater steric interaction than the two CH groups in pyridine *N*-oxide. The greatly increased steric effect expected from the α-CH_3 in 2-methylpyridine is manifested in much reduced adduct stability and correspondingly lower enthalpy of adduct formation, compared with the other heterocyclic bases.

Calorimetric titration data for the reaction of $[Eu(fod)_3]$ with five heterocyclic bases and dimethyl sulphoxide could not be fitted to computed thermograms if 1 : 1 reaction was assumed, but excellent fits were obtained when successive addition of two base molecules was assumed, according to equations (3) and (4). This is

$$[Eu(fod)_3] + \text{base} \rightleftharpoons [Eu(fod)_3(base)] \quad (3)$$

$$[Eu(fod)_3(base)] + \text{base} \rightleftharpoons [Eu(fod)_3(base)_2] \quad (4)$$

* Throughout this paper: 1 Torr = (101 325/760) Pa.

a similar reaction scheme to that observed by fluorescence spectroscopy for the reaction of $[Eu(fod)_3]$ with amines.[11] A typical example of the fit of experimental points to computed thermograms is shown in Figure 1 and complete thermodynamic data for the reactions are given in Table 3.

As has been observed qualitatively, the adducts are slightly more stable than those with $[Eu_2(tmhd)_6]$, although the difference is less than might be expected and, in any case, the data are not strictly comparable because of the different stoicheiometries. For the formation of the adducts with heterocyclic bases, the enthalpy of desolvation would account for the unusually small enthalpy change associated with addition of the first molecule of base.

Addition of the second molecule of base is associated with a rather large enthalpy change and is strongly entropy resisted, suggesting that little additional solvent displacement occurs in this stage.

The results obtained for dimethyl sulphoxide differ significantly from those obtained with heterocyclic bases. The two successive adduct-formation constants are now about equal, as are the two enthalpy changes. In both steps the associated entropy changes are positive, al-

TABLE 3

Thermodynamic data for the successive reactions $[Eu(fod)_3]$ + base $\rightleftharpoons$ $[Eu(fod)_3(base)]$ and $[Eu(fod)_3(base)]$ + base $\rightleftharpoons$ $[Eu(fod)_3(base)_2]$ in benzene solution at 30 °C

Base	[Eu]/ mmol dm^{-3}	log(K_1/ dm^3 mol^{-1})	log(K_2/ dm^3 mol^{-1})	$-\Delta H_1^\ominus$	$-\Delta H_2^\ominus$	$-\Delta G_1^\ominus$	$-\Delta G_2^\ominus$	$\Delta S_1^\ominus$	$\Delta S_2^\ominus$
				kJ mol^{-1}				J K^{-1} mol^{-1}	
Pyridine	0.5—1.5	4.0 ± 0.3	2.7 ± 0.3	17 ± 1	36 ± 5	23.2 ± 1.7	15.7 ± 1.7	+21 ± 9	−68 ± 22
4Me-py	0.5—3.2	4.3 ± 0.3	3.0 ± 0.3	18 ± 1	33 ± 3	24.9 ± 1.7	17.4 ± 1.7	+23 ± 9	−51 ± 16
3Me-py	0.5—3.2	4.3 ± 0.3	3.0 ± 0.3	15 ± 2	29 ± 1	24.9 ± 1.7	17.4 ± 1.7	+33 ± 12	−39 ± 16
2Me-py	2.5—5.8	2.5 ± 0.3	1.6 ± 0.3	11 ± 1	42 ± 4	14.5 ± 1.7	9.3 ± 1.7	+12 ± 9	−108 ± 19
2,4,6Me$_3$-py	2.2—4.2	1.0 ± 0.3	0.5 ± 0.3	7 ± 1	35 ± 2	5.8 ± 1.7	2.9 ± 1.7	−4 ± 9	−107 ± 12
dmso	1.8—3.0	3.3 ± 0.3	3.3 ± 0.3	15 ± 1	15 ± 3	19.1 ± 1.7	19.1 ± 1.7	+14 ± 9	+14 ± 16

$K_1 > K_2$, as is commonly observed in two-step systems and explained by statistical effects. Methyl substitution in pyridine at the 3- or 4-position leads to small increases in adduct stabilities, as in many other systems, presumably due to inductive effects, but methyl substitution in the 2-position leads to large decreases in adduct stabilities due to steric interference; this is particularly marked in the case of 2,4,6-trimethylpyridine (2,4,6Me$_3$-py), where both carbon atoms adjacent to the nitrogen-donor atom are substituted.

Enthalpies of adduct formation are comparable in magnitude to those in other similar systems, but are not though small. The implication is that solvent displacement is now about equally divided between the two steps. This difference between dimethyl sulphoxide and the heterocyclic bases is consistent with the steric properties of dimethyl sulphoxide, in which the isolated *O*-donor atom could be expected to contribute less to solvent displacement than the N atom in pyridine bases.

$[Pr(fod)_3]$.—Stoicheiometrically, $[Pr(fod)_3]$ was found to behave in the same way as the corresponding europium compound, adducts of the form $[Pr(fod)_3(base)]$ and $[Pr(fod)_3(base)_2]$ being formed successively. Cryoscopic measurements gave values of m.w./f.w. from 0.96 to 1.07

TABLE 4

Thermodynamic data for the successive reactions $[Pr(fod)_3]$ + base $\rightleftharpoons$ $[Pr(fod)_3(base)]$ and $[Pr(fod)_3(base)]$ + base $\rightleftharpoons$ $[Pr(fod)_3(base)_2]$ in benzene solution at 30 °C

Base	[Pr]/ mmol dm^{-3}	log(K_1/ dm^3 mol^{-1})	log(K_2/ dm^3 mol^{-1})	$-\Delta H_1^\ominus$	$-\Delta H_2^\ominus$	$-\Delta G_1^\ominus$	$-\Delta G_2^\ominus$	$\Delta S_1^\ominus$	$\Delta S_2^\ominus$
				kJ mol^{-1}				J K^{-1} mol^{-1}	
Pyridine	1.8—5.4	3.3 ± 0.3	3.0 ± 0.3	24 ± 2	9 ± 2	19.1 ± 1.7	17.4 ± 1.7	−17 ± 14	+28 ± 13
4Me-py	1.6—3.3	4.3 ± 0.3	3.0 ± 0.3	24 ± 1	13 ± 1	24.9 ± 1.7	17.4 ± 1.7	+2 ± 9	+14 ± 13
3Me-py	1.7—3.5	4.0 ± 0.3	3.0 ± 0.3	18 ± 2	13 ± 1	23.2 ± 1.7	17.4 ± 1.7	+17 ± 14	+15 ± 6
2Me-py	1.7—4.1	3.0 ± 0.3	2.0 ± 0.3	11 ± 1	20 ± 1	17.4 ± 1.7	11.6 ± 1.7	+20 ± 9	−29 ± 7

equally distributed between the two steps: in each case the enthalpy change is much smaller in the first step; that this is observed independently in all five systems makes it unlikely that it is an experimental error. In every case except that of 2,4,6-trimethylpyridine the first step in base addition is accompanied by a positive entropy change and in the case of 2,4,6Me$_3$-py, where the large steric effect of the two α-methyl groups could be expected to lead to a large negative entropy change, the entropy change, although negative, is extremely small. The first step in base addition is thus entropy driven, suggesting that this step is accompanied by displacement of a large solvation sheath; such a sheath is consistent with the observed high solubility of the fod complex and in the concentration range 1.8×10^{-2}—3.6×10^{-2} mol dm^{-3} for $[Pr(fod)_3]$ in benzene. Thermodynamic data for adduct formation are given in Table 4.

Comparison of Tables 3 and 4 reveals both similarities and differences between the results for $[Eu(fod)_3]$ and $[Pr(fod)_3]$. For $[Pr(fod)_3]$ as for $[Eu(fod)_3]$, $K_1 > K_2$ and the steric effect of α substitution by methyl groups leads to lower adduct stabilities, particularly to lower K_2. The enthalpy changes associated with addition of the first base molecule are similar to those found with $[Eu(fod)_3]$ and in most cases this step in the reaction is also associated with a positive entropy change. There is, however, a marked difference between the two systems in the second step of the reaction: in the praseodymium

series $-\Delta H_2 < -\Delta H_1$ (except for 2-methylpyridine) and the second step of the reaction is also associated with a positive entropy change. This difference becomes very apparent if the total enthalpy changes, $\Delta H_1 + \Delta H_2$ (which are the most accurate of all the measurements), are compared: for the europium series the total enthalpy change is *ca.* -50 kJ mol^{-1} and for the praseodymium series *ca.* -33 kJ mol^{-1}. At the same time the total entropy changes, $\Delta S_1 + \Delta S_2$, are large and negative for the sterically unhindered europium systems (average -50 J K^{-1} mol^{-1}) but are positive for the corresponding praseodymium systems (average $+20$ J K^{-1} mol^{-1}).

The implication of these differences between the two series of results is that [Pr(fod)$_3$] is more extensively solvated than [Eu(fod)$_3$], so that when base adducts are formed more solvent displacement occurs and this is reflected in a more positive entropy change and a reduced enthalpy change. Furthermore, the difference mainly occurs in the second step of the reaction.

[Pr(tmhd)$_3$].—We were unable to obtain reproducible calorimetric titration data with this compound. Cryoscopic molecular-weight determinations gave values of m.w./f.w. of 0.5—0.8 in the concentration range 7×10^{-3} to 1.3×10^{-2} mol dm^{-3}. We conclude that this compound is even more sensitive to trace amounts of water; it is also experimentally more difficult to use because of its very low solubility.

Conclusions.—The reproducibility of results for individual systems and the consistency of comparative results for different systems indicate that the combination of azeotropic drying and calorimetric titration provides a satisfactory method for obtaining quantitative data for these experimentally difficult reactions. It has the added advantage of providing reliable enthalpy data.

The results reveal a variety of stoicheiometries, depending on the position of the lanthanide in the series and on the β-diketone. While the results obtained with tmhd complexes are comparable with those obtained with β-diketone derivatives of other metals, the fluorinated lanthanide shift reagents react much more strongly with bases.

The effect of fluorination, which greatly increases the solubility of the reagents, is, however, not simply to increase the Lewis acidity; thus, for example, K_1 for the reaction of [Eu(fod)$_3$] with pyridine is not significantly different from K for the reaction of [Yb(tmhd)$_3$] with the same base. Fluorination leads to the addition of two molecules of base instead of one and, most remarkably, the addition of the first molecule of base is accompanied by a positive entropy change. This presumably arises from displacement of an extensive solvation envelope and suggests that the improved performance of the fluorinated shift reagents has as much to do with their interaction with the solvent as with their interaction with the organic substrate.

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