Calorimetric Titration and Hydrogen-1 Nuclear Magnetic Resonance Studies of Adduct Formation Between Cobalt(III) β-Diketonates and a Lanthanide Shift Reagent

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Titration calorimetry has been used to study the reaction of the lanthanide shift reagent [Eu(fod)$_3$], tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)europium(III), with tris(β-diketonato)cobalt(III) complexes of pentane-2,4-dione (Hacac), benzoylacetone (Hbzac), and dibenzoylmethane (Hdbm) in benzene. Complementary ^{1}H n.m.r. studies have also been performed. In accord with previous results, symmetrical 1 : 1 adduct formation involving three oxygen bridges to [Eu(fod)$_3$] occurs for the first two complexes. For [Co(acac)$_3$], a $\Delta H^\ominus$ value of -30.5 ± 1.2 kJ mol^{-1} and a K value of $\geqslant 10^4$ dm^3 mol^{-1} were obtained. For *fac*-[Co(bzac)$_3$], the $\Delta H^\ominus$ value is approximately zero with $K \geqslant 10^3$ dm^3 mol^{-1}; hence the aryl functions are quite effective in reducing the donor capacity of the bridging oxygens in this case. In contrast, the calorimetric and n.m.r. studies indicate that there is no adduct formation by [Co(dbm)$_3$], a result which apparently reflects steric shielding by the aryl groups of the oxygen-donor atoms of this complex.

As part of an extended study of the interaction of lanthanide shift reagents (l.s.r.s) with metal complexes,[1-3] kinetic, thermodynamic, and structural aspects of the interaction of tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)europium(III), [Eu(fod)$_3$], with a series of tris(β-diketonato)cobalt(III) complexes have been investigated.[3] Hydrogen-1 n.m.r. studies clearly indicate that tris(pentane-2,4-dionato)cobalt(III), [Co(acac)$_3$], and tris(benzoylacetonato)cobalt(III), [Co(bzac)$_3$], both react with l.s.r. to yield 1 : 1 adducts in $CDCl_3$. From the n.m.r. spectra it was inferred that adduct formation takes place along the C_3 axes of the respective cobalt complexes such that a symmetrical l.s.r. adduct containing three bridging oxygens to the europium ion is formed in each case. The respective adducts have been crystallised and physical measurements [2,3] (including an *X*-ray diffraction study) [2] indicate that the proposed solution structures persist in the solid state. In contrast to simple substrate–l.s.r. systems,[4] slow chemical exchange on the n.m.r. time scale occurs for these systems; n.m.r. signals resulting from both the free cobalt complex as well as its adduct with [Eu(fod)$_3$] are observed simultaneously at ambient temperature.[3]

As an extension of the above investigation, parallel calorimetric studies of the interaction of [Eu(fod)$_3$] with the above two cobalt complexes as well as with tris(dibenzoylmethanato)cobalt(III), [Co(dbm)$_3$], are now reported.

EXPERIMENTAL

The compound [Eu(fod)$_3$] (Aldrich) and its deuteriated derivative [Eu([^{2}H$_9$]fod)$_3$] (Merck, Sharp, and Dohme Ltd.) were dried as described previously.[3] Benzene ('crystallisable, sulphur-free') from 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. Deuteriated benzene (Koch Light) was dried over Linde 3A molecular sieves before use. Calorimetric titrations were carried out at 30 °C in a LKB 8700 calorimeter, using the previously described technique.[5] Enthalpograms were obtained by plotting the cumulative heat of reaction, after correcting for dilution effects, against the total concentration of cobalt complex. Three titrations at different concentrations of l.s.r. in the range 0.5×10^{-3}—3.0×10^{-3} mol dm^{-3} were performed for each system. The benzene solutions were prepared by weighing the appropriate amount of l.s.r. and dissolving it in pure toluene (*ca.* 10 cm^3); traces of water were then removed azeotropically by distillation of the toluene on to phosphorus pentaoxide in an atmosphere of dry nitrogen, until the residual volume was less than 1 cm^3. This 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 cobalt complex at a concentration of *ca.* 100 times that of the solution of shift reagent.

The conditions used for the n.m.r. experiments were the same as described previously; [3] all operations involving transfer of the dried l.s.r. were performed in a glove-box under dry nitrogen.

RESULTS AND DISCUSSION

Preliminary calorimetric experiments were performed in chloroform but high heats of solvation in this solvent resulted in data of low reliability. However, on using benzene, heats of solvation were lower and the calorimetric studies were performed using this solvent. Cryoscopic molecular-weight determinations indicate that [Eu(fod)$_3$] is monomeric in benzene in the concentration range 1.1×10^{-2}—3.0×10^{-2} mol dm^{-3},[6] and hence self-association effects of the type found for this l.s.r. in carbon tetrachloride [7] can be ignored in the present study. For each system studied, a solution of [Eu(fod)$_3$] was titrated with complex solution and the heat changes monitored over the course of the titration. Figure 1 shows the result of one titration for [Co(acac)$_3$]; extrapolation of the linear portions of the plot confirm a 1 : 1 stoicheiometry for adduct formation in this case. A stability constant for adduct formation of $\geqslant 10^4$ dm^3 mol^{-1} can be estimated directly from this plot and a value for $\Delta H^\ominus$ of -30.5 ± 1.2 kJ mol^{-1} was calculated from the total heat released during the titration.

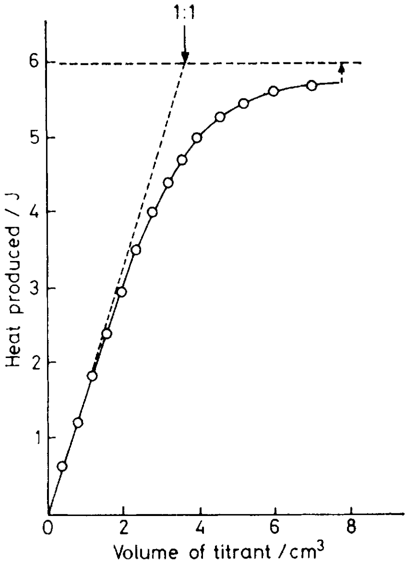

FIGURE 1 Calorimetric titration of [Co(acac)$_3$] in benzene (0.50 mol dm^{-3}) into [Eu(fod)$_3$] (100 cm^3) in benzene (1.82 mmol dm^{-3}) at 30 °C

Parallel ^{1}H n.m.r. studies have been performed and the changes in the spectrum of [Co(acac)$_3$] in C_6D_6 on addition of [Eu([$^2H_9$]fod)$_3$] are similar to those observed previously when $CDCl_3$ was used as solvent.[3] As [Eu([$^2H_9$]fod)$_3$] is added the intensities of the signals arising from the free cobalt complex decrease, together with a concomitant rise of new signals for the adduct. Relative to tetramethylsilane, the adduct signals (δ/p.p.m. values) occur at -6.18 (CH_3 adjacent to site of attachment of l.s.r.), 4.21 (other CH_3), 5.91 (–CH= of l.s.r. in adduct), and 6.12 (–CH= of cobalt complex in adduct). At a 1 : 1 ratio of l.s.r. : complex no signals corresponding to free [Co(acac)$_3$] remain. A K value of $>10^4$ dm^3 mol^{-1} can be estimated for this system from the spectral changes; as expected, this value is larger than that obtained (830 ± 300 dm^3 mol^{-1})[3] when the experiment was carried out using $CDCl_3$ (which has a higher solvating ability).

The results of calorimetric titrations involving *fac*-[Co(bzac)$_3$] and [Co(dbm)$_3$] in C_6H_6 are summarised in the Table. Approximately zero heat changes occurred for each system and thus either adduct formation is insignificant or $\Delta H^\ominus$ for adduct formation is near zero for these cases. The latter situation appears to be the case for the *fac*-[Co(bzac)$_3$] system since the changes in the ^{1}H n.m.r. spectrum of this complex in C_6D_6 on incremental addition of [Eu([$^2H_9$]fod)$_3$] clearly indicate 1 : 1 adduct formation (Figure 2). The reaction is thus entropy controlled presumably as a result of substantial desolvation on adduct formation. The K value of $\geqslant 10^3$ dm^3 mol^{-1} is once again higher than the value of 530 ± 150 dm^3 mol^{-1} obtained previously[3] when $CDCl_3$ was used as solvent. From the n.m.r. and calorimetric results it is apparent that the aryl groups are quite effective in reducing the Lewis basicity of the oxygen donors of *fac*-[Co(bzac)$_3$] relative to [Co(acac)$_3$].

Thermodynamic data for the interaction of [Eu(fod)$_3$] with the cobalt complexes

	Calorimetry[a]		^{1}H N.m.r.[b]
System	$-\Delta H^\ominus$/ kJ mol^{-1}	K/ dm^3 mol^{-1}	K/ dm^3 mol^{-1}
[Co(acac)$_3$] + [Eu(fod)$_3$]	30.5 ± 1.2[c]	10^4	$\geqslant 10^4$
[Co(bzac)$_3$] + [Eu(fod)$_3$]	1 ± 1		$\geqslant 10^3$
[Co(dbm)$_3$] + [Eu(fod)$_3$]	*d*		*ca.* 0[e]

[a] In C_6H_6 at 30 °C. [b] In C_6D_6 at 33 °C. [c] Mean deviation. [d] No heat change detected. [e] No evidence of adduct formation.

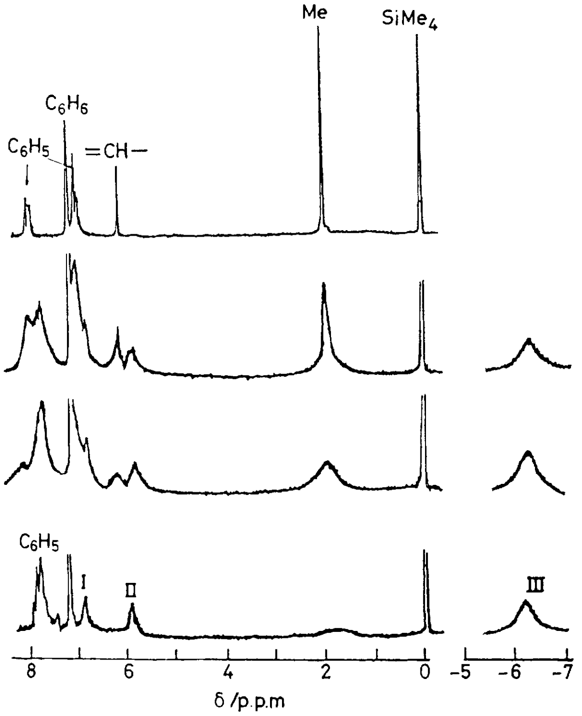

FIGURE 2 Selected ^{1}H n.m.r. spectra showing the effect of addition of [Eu([$^2H_9$]fod)$_3$] (L) on *fac*-[Co(bzac)$_3$] (S) in C_6D_6 at 33 °C, [S] = 0.07 mol dm^{-3} (*a*), [L]/[S] = 0.48 (*b*), [L]/[S] = 0.67 (*c*), and [L]/[S] = 1.20 (*d*). I = –CH= of cobalt complex in adduct, II = –CH– of [Eu([$^2H_9$]fod)$_3$] in adduct, and III = CH_3 of cobalt complex in adduct

In contrast to the above systems, the approximately zero heat change observed for [Co(dbm)$_3$] reflects the absence of adduct formation since no change in the n.m.r. spectrum of this complex in C_6D_6 occurred on addition of excess of [Eu([$^2H_9$]fod)$_3$]. This lack of adduct formation has been attributed to the presence of bulky aryl groups which effectively block all the oxygen-donor sites and prevent interaction with the l.s.r.[3]

For the three cobalt complexes investigated the calorimetric and n.m.r. results are thus in complete accord.

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