Nuclear Magnetic Resonance Study of the Interaction of Lanthanide Shift Reagent with Tris(β-diketonato)cobalt(III) Complexes. Kinetics of Adduct Formation Involving Slow Chemical Exchange at Ambient Temperature

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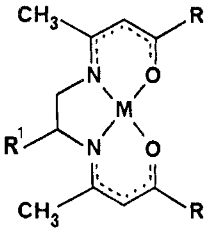
Abstract: Reaction of the lanthanide shift reagent (LSR), Eu(fod)$_3$, with a series of tris(β-diketonato)cobalt(III) complexes in CDCl$_3$ leads to 1:1 adduct formation in each case. Unlike simple substrate–LSR systems, slow chemical exchange with respect to the NMR time scale occurs and NMR signals resulting from both the free cobalt complex as well as its adduct with Eu(fod)$_3$ are observed simultaneously at ambient temperature. Two of the adducts have been isolated and characterized; adduct formation occurs along a C$_3$ axis of the cobalt complex such that three β-diketone oxygen atoms (around one face of the octahedron) bridge to the LSR. Estimates of the adduct formation constants have proved possible. Bulky terminal alkyl or aryl groups on the β-diketone ligand in the complex can inhibit adduct formation by sterically blocking both the faces incorporating three donor oxygens. As observed previously for other europium systems, the lanthanide-induced shifts for the adduct are proportional to T^{-1}. The kinetics and mechanism of dissociation of the adducts have been investigated—the dissociation is first order and lifetimes for two of the adducts are of the order of 10^{-2} s. Relative to the lifetimes of other LSR–substrate systems where there is only a single donor site on the substrate, the lifetimes found for the present adducts are unusually long.

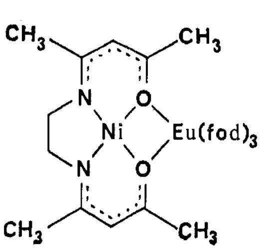
Introduction

The interaction of lanthanide shift reagents (LSRs) such as Eu(fod)$_3$ or Pr(fod)$_3$ with organic substrates has been extensively investigated[1,2] but their interaction with inorganic coordination complexes has received only limited attention.[3] In previous studies it has been demonstrated that LSRs can be used successfully to induce shifts in the NMR spectra of a series of diamagnetic metal complexes of type I.[4] The LSR interacts with the lone-pair electron density of the cis oxygen donors to yield 1:1 adducts of which II is typical. By choice of appropriately substituted complexes of type I[5] it has been possible to demonstrate the influence of both steric and electronic effects on the lanthanide-induced shifts;[4] for example, when R is a bulky alkyl group (such as *tert*-butyl) or an electron-withdrawing group (such as CF$_3$), adduct formation is inhibited. The technique has formed the basis for a conformational study of the backbone derived from propylenediamine in I (M = Ni; R = CH$_3$; R′ = CH$_3$) and this complex as well as other related complexes incorporating chiral centers gave the predicted spectral changes when reacted with an optically active LSR. The kinetics of dissociation of several of the above LSR adducts have been studied and in all cases fast exchange between the free metal complex and the LSR adduct occurs,[6] although the lifetimes of the adducts are generally longer than the lifetimes reported for other LSR–organic substrate adducts in which the organic substrate has only one site available for attachment to the LSR.[7] As an extension of the previous studies mentioned above, we now present the results of an investigation involving a series of metal complexes which are potentially capable of presenting three oxygen donors simultaneously to the LSR. The complexes chosen were a series of tris(β-diketonato)cobalt(III) complexes, for such complexes have two sets of three oxygen donors suitably oriented for coordination to the LSR, are diamagnetic, kinetically inert, give simple NMR spectral patterns, and exhibit the necessary solubility in nonpolar solvents such as CDCl$_3$.



M = Ni, Pd, Pt
R = alkyl substituent
R′ = H or CH$_3$

I



II

Experimental Section

Reagents. Eu(fod)$_3$ and Pr(fod)$_3$ were obtained from Pierce Chemical Co. and Eu(fod-d_9)$_3$ and Pr(fod-d_9)$_3$ were obtained from Nuclear Magnetic Resonance Ltd. The purity of each batch of Eu(fod)$_3$ and Pr(fod)$_3$ was checked by NMR spectroscopy. The ^{1}H NMR spectra of these shift reagents exhibited a single sharp symmetrical peak for the *tert*-butyl groups and no additional *tert*-butyl resonance appeared during the respective shift reagent runs. This is a reliable criterion of adequate purity for use of these reagents for quantitative measurements.[8] The deuterated reagents Eu(fod-d_9)$_3$ and Pr(fod-d_9)$_3$ each showed only a singlet for the -CH= proton; no *tert*-butyl resonance was observed. Deuterated chloroform (Koch Light Laboratories) was stored over freshly dried anhydrous sodium bicarbonate to remove any phosgene or hydrogen chloride[9] and was dried over Linde 3A molecular sieves before use.[9]

The metal complexes were prepared by published methods[10] and in most cases purified by column chromatography. Their purity was checked by NMR spectroscopy as well as by elemental analysis. The facial-cis isomers used for the study were separated from the trans forms by thick layer chromatography (on silica gel, Merck G, type 60). The β-diketone ligands were either obtained commercially or were prepared by known procedures.[11]

Experimental Procedures. Water coordinates strongly to the lanthanide shift reagents;[12,13] hence all shift reagents were dried at approximately 120 °C in vacuo over P$_2$O$_5$ for 2 days before use to yield the anhydrous reagents.[12,13] Considerable care was taken not to expose

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the dry shift reagents to the atmosphere as they pick up water almost instantaneously.[13] All operations involving transfer of the dry shift reagents were performed in a glovebox filled with dry nitrogen. All glassware was preheated in an air oven and kept in a desiccator before use.

The shift reagent runs were performed in the following manner. The metal complex was dissolved in 0.5 mL of $CDCl_3$ in the NMR tube (solution concentration 0.05-0.1 M). Solid lanthanide shift reagent was then added directly (under dry N_2 atmosphere) to the solution in the tube. The tube was capped and the solution was then mixed thoroughly. The spectrum was recorded after allowing 5 min for the solution to reach thermal equilibrium inside the NMR probe. The weight of lanthanide shift reagent added to the NMR tube was obtained by difference weighing. The time between successive LSR additions was 15-30 min.

Kinetic data were obtained by means of temperature-dependent line-broadening studies; a series of NMR spectra of a solution containing a known concentration of substrate and shift reagent were obtained at a number of temperatures between −60 and 50 °C. The temperature of the NMR probe was checked before and after each spectrum was run (using an NMR probe thermometer for temperatures above −30 °C). Temperatures quoted are accurate to ±1 °C. A linear least-squares computer program was used for the activation parameter plots.

All the NMR spectra were recorded at 100 MHz using a JEOL JNM-NH-100 spectrometer. Unless otherwise stated, measurements were made at the normal probe temperature of 33 °C. Chemical shifts are relative to tetramethylsilane (Me_4Si) as internal standard. Line widths were accurately measured from expanded NMR spectra. The shift reagents runs were each performed at least three times and the respective observed line widths averaged.

For use in calculation of equilibrium constants, several manual integrations using squared paper were performed for each set of spectra and the results meaned. Because of the inherent broadness of the peaks, this method was found to be more accurate for estimating relative peak intensities than use of the integrator incorporated in the JEOL spectrometer.

Tris(2,4-pentanedionato)cobalt(III) Tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-1,4,6-octanedionato)europium(III) Hemibenzene $Co(acac)_3$–$Eu(fod)_3 \cdot \frac{1}{2}C_6H_6$. The dark green adduct was recrystallized from benzene and then stored in a desiccator over P_2O_5. NMR spectroscopy confirmed the presence of benzene; the amount of benzene was estimated from the intensity of its peak in the spectrum relative to that of a CH_3 peak of the adduct. Anal. Calcd for $Co(C_5H_7O_2)_3$-$Eu(C_{10}H_{10}O_2F_7)_3 \cdot \frac{1}{2}C_6H_6$: C, 40.40; H, 3.78; C_6H_6, 2.72; Co, 4.12. Found: C, 40.22; H, 4.01; C_6H_6, 3.0; Co, 4.08.

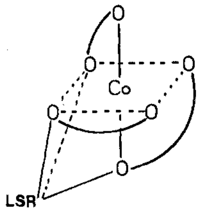
Tris(3-chloro-2,4-pentanedionato)cobalt(III) Tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium(III) Hemibenzene, $Co(acacCl)_3$–$Eu(fod)_3 \cdot \frac{1}{2}C_6H_6$. The dark green adduct was recrystallized from benzene, then stored in a desiccator over P_2O_5. NMR spectroscopy confirmed the presence of benzene. Anal. Calcd for $Co(C_5H_6O_2Cl)_3$-$Eu(C_{10}H_{10}O_2F_7)_3 \cdot \frac{1}{2}C_6H_6$: C, 37.54; H, 3.34; C_6H_6, 2.54. Found: C, 37.23; H, 3.35; C_6H_6, 2.9.

Results and Discussion

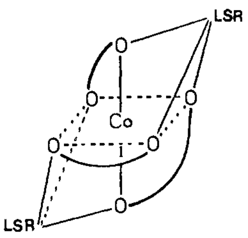
The Nature of the Interaction. There are several changes in the NMR spectrum of tris(pentane-2,4-dionato)cobalt(III), $Co(acac)_3$, when $Eu(fod)_3$ is added incrementally. The spectral changes clearly indicate that adduct formation between $Co(acac)_3$ and $Eu(fod)_3$ occurs. On addition of $Eu(fod)_3$ to a solution of the complex in $CDCl_3$, the intensities of the original methyl and the -CH= signals resulting from $Co(acac)_3$ decrease and broaden while five new signals appear. As further $Eu(fod)_3$ is added these latter signals increase in intensity and there is a concomitant decrease in intensity of the original peaks. When greater than a 1:1 molar ratio of $Eu(fod)_3$ is reached only the five new signals together with further signals contributed by free $Eu(fod)_3$ are present. Separate resonances resulting from both the adduct and the free substrate clearly indicate that slow exchange takes place between the adduct and substrate at 33 °C. In contrast, for previous LSR studies involving simple organic substrates, chemical exchange between free and complexed substrate has almost invariably been fast when the experiments were performed at ambient NMR probe temperatures,[1] although isolated examples of slow exchange at low temperatures have been reported.[9,14,15]

In order to aid assignment of the new signals, the experiment was repeated using $Eu(fod\text{-}d_9)_3$ which contains only the -CH= sites nondeuterated. Both sets of spectra (arising from the nondeuterated and deuterated LSRs) were similar except that a strong, broad signal at 3.38 ppm in the former was absent in the latter. This signal was thus assigned to the *tert*-butyl protons of the $Eu(fod)_3$ portion of the adduct. The observed spectral changes for the interaction with $Eu(fod\text{-}d_9)_3$ are illustrated in Figure 1. In this case when greater than a 1:1 mole ratio of LSR to $Co(acac)_3$ is present then only four new signals together with a -CH= signal from free $Eu(fod\text{-}d_9)_3$ are observed.

Assuming that a symmetrical adduct is formed, then coordination to the LSR may occur via the β-diketone oxygen atoms at one or both available octahedral faces of $Co(acac)_3$ (that is, along the C_3 axis) to form either a 1:1 adduct of type III or a 2:1 adduct of type IV. In each case the europium(III) has a coordination number of nine—a common coordination number for this ion.[16,17] The postulated bridging situation is not unexpected as other examples of polynuclear β-diketone complexes which contain sets of three bridging oxygen donors have been reported previously.[18]



III



IV

If we ignore possible self-association effects of the LSR then two main equilibria may be involved:[8,12]

$$L + S \underset{}{\overset{K_1}{\rightleftharpoons}} LS \qquad K_1 = \frac{[LS]}{[L][S]} \tag{1}$$

$$LS + L \underset{}{\overset{K_2}{\rightleftharpoons}} L_2S \qquad K_2 = \frac{[L_2S]}{[LS][L]} \tag{2}$$

where L = lanthanide shift reagent and S = substrate. The occurrence of four signals for the adduct suggests that it has a 1:1 stoichiometry; in this case the methyl groups of each pentane-2,4-dionato ligand are in different environments[19] and hence two methyl signals as well as two =CH- signals [one from $Co(acac)_3$ and one from the LSR] would be expected. In contrast, for 2:1 adduct formation, only three adduct signals would be expected. The relative intensities of the four signals for the adduct were found to be 1:1:3:3. This ratio remained constant throughout the run (except where spectral overlap occurs) and is the ratio expected for 1:1 adduct formation. In a further experiment, the ratio of the sum of the intensities of all methyl signals arising from $Co(acac)_3$ to that of a reference $CHCl_3$ peak was monitored at each LSR concentration. Within experimental error, the ratio remained constant throughout the run.

The constant 1:1:3:3 ratio of the observed signals, together with the absence of any unaccounted-for methyl intensity, provides strong evidence that, under the conditions of the experiment, 2:1 adduct formation is insignificant.[20]

In order to investigate further the unusual behavior observed for $Co(acac)_3$, parallel studies involving the related Co(β-diketonato)$_3$ complexes V-VIII were undertaken. The facial (cis) isomers of VII and VIII were isolated and used for the study.

Table I. Chemical Shifts (ppm) of Adduct NMR Signals (Relative to Me_4Si) at 33 °C

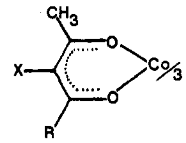
adduct	CH_3[a]	R[b]	H[c]	H (fod)
$Co(acac)_3$–Eu(fod-d_9)$_3$	−6.80[d]	4.52	6.09	5.62
$Co(acacCl)_3$–Eu(fod-d_9)$_3$	−8.92	5.45		5.03
$Co(acacBr)_3$–Eu(fod-d_9)$_3$	−9.00	5.58		5.03
$Co(bzac)_3$–Eu(fod-d_9)$_3$	−6.74	*e*	6.89	5.59
Co(*t*-Buac)$_3$–Eu(fod-d_9)$_3$	−6.37	2.95	6.19	5.81

[a] CH_3 adjacent to the site of attachment of Eu(fod-d_9)$_3$. [b] For acac, acacCl, acacBr, R = CH_3; for bzac, R = C_6H_5; for *t*-Buac, R = $(CH_3)_3C$. [c] -CH═ of complexed Co(β-diketonato)$_3$. [d] Negative values indicate high-field side of Me_4Si. [e] Aromatic proton resonances at ~10.26 and ~8.34 ppm.

Table II. Lanthanide-Induced Shifts (δΔ, ppm) of Adduct Resonances Relative to Corresponding Resonances in Free Substrate at 33 °C

adduct	CH_3[a]	R
$Co(acac)_3$–Eu(fod-d_9)$_3$	−8.99	2.34 (CH_3)
$Co(acacCl)_3$–Eu(fod-d_9)$_3$	−11.37	3.00 (CH_3)
$Co(acacBr)_3$–Eu(fod-d_9)$_3$	−11.54	3.04 (CH_3)
Co(*t*-Buac)$_3$–Eu(fod-d_9)$_3$	−8.52	2.13 (*t*-Bu)
$Co(bzac)_3$–Eu(fod-d_9)$_3$	−9.06	2.31, 0.90 (C_6H_5)

[a] CH_3 adjacent to the site of attachment of Eu(fod-d_9)$_3$; negative values indicate an upfield shift.



(V) R = CH_3, X = Cl: $Co(acacCl)_3$
(VI) R = CH_3, X = Br; $Co(acacBr)_3$
(VII) R = C_6H_5, X = H; $Co(bzac)_3$
(VIII) R = $C(CH_3)_3$, X = H; Co(*t*-Buac)$_3$

The changes in the NMR spectra of the complexes V–VIII on the incremental addition of Eu(fod-d_9)$_3$ are in accord with those observed for the interaction of this LSR with $Co(acac)_3$. In each case the signals had the expected relative intensities for 1:1 adduct formation. It is significant that when the cobalt complex of a β-diketone in which both R groups are bulky (namely, dibenzoylmethanato or dipivaloylmethanato) was used for similar experiments, no interaction with Eu(fod-d_9)$_3$ of the type discussed above was observed. This lack of interaction is most readily rationalized in terms of increased steric hindrance about both sets of three oxygens at which coordination could occur. A related steric inhibition of adduct formation has been shown to occur with complexes of type I for which R is a bulky alkyl or aryl group.[4]

The assignment of the Eu(fod-d_9)$_3$ adduct signals for the various cobalt complexes (Table I) becomes straightforward once 1:1 adduct formation is concluded. A comparison of the respective lanthanide-induced shifts for the various terminal R groups is tabulated in Table II. The chemical shifts of the adduct signals are virtually independent of Eu(fod-d_9)$_3$ concentration. The positions of the methyl resonance in the adduct of *cis*-$Co(bzac)_3$ (−6.74 ppm) and of the corresponding resonance in the adduct of *cis*-Co(*t*-Buac)$_3$ (−6.37 ppm) confirm that the methyl groups adjacent to the oxygen donors are the ones which give rise to the high-field signals. Similarly, comparison of the spectrum of the adduct of $Co(acacCl)_3$ with the corresponding spectra of the other cobalt complexes has aided the assignment of the respective -CH═ resonances listed in Table I.[21]

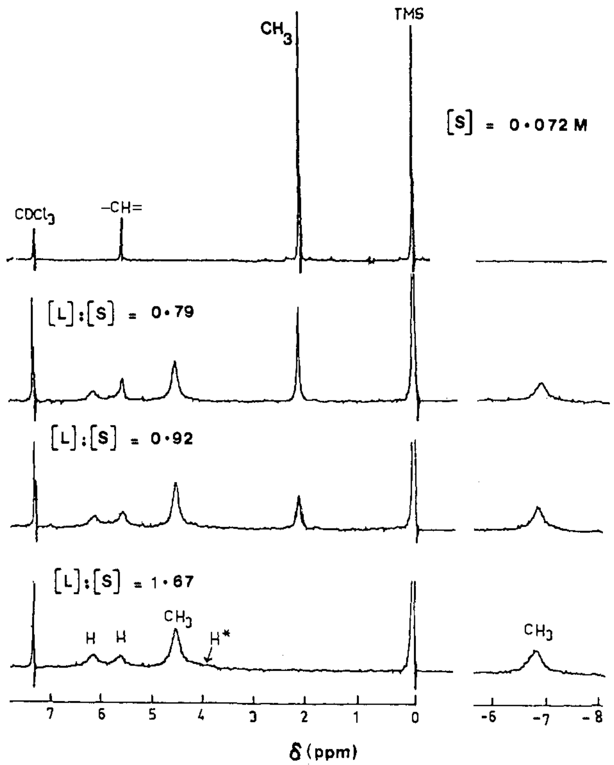


Figure 1. Selected NMR spectra showing the effect of addition of Eu(fod-d_9)$_3$ to $Co(acac)_3$ in $CDCl_3$; L = Eu(fod-d_9)$_3$, S = $Co(acac)_3$. Asterisk indicates signal from -CH═ of uncomplexed Eu(fod-d_9)$_3$.

Isolation and Characterization of Adducts. The solid adducts, $Co(acac)_3$–$Eu(fod)_3$ and $Co(acacCl)_3$–$Eu(fod)_3$, crystallized on slow evaporation of the $CDCl_3$ solution at the end of the respective NMR runs. The solids were recrystallized from benzene and elemental analyses confirmed their 1:1 stoichiometry; after recrystallization each product had 0.5 mol of benzene associated with it.[22]

The infrared spectra of the adducts exhibit characteristic absorption bands arising from the particular substrate as well as the LSR; these bands show only minor frequency shifts from their corresponding positions for the free precursors. Similarly, there is little change in the visible spectrum of each cobalt complex (in chloroform) on adduct formation. A wide sweep NMR spectrum of $Co(acac)_3$–$Eu(fod)_3$·½C_6H_6 redissolved in $CDCl_3$ is illustrated in Figure 2. This spectrum is in complete accord with the spectra obtained after successive additions of $Eu(fod)_3$ to $Co(acac)_3$ and which were discussed earlier; the assignments given in Figure 2 are based on the results from the previous study.[23]

The above evidence strongly suggests that the coordination shell of the cobalt complex remains intact on adduct formation and, indeed, the known kinetic inertness of cobalt(III) complexes makes ligand exchange (within the time of the experiment) extremely unlikely. An X-ray crystal structure analysis of $Co(acac)_3$–$Eu(fod)_3$·½C_6H_6 confirms that this is so.[24] The adduct consists of an octahedral arrangement of acac oxygens around the cobalt atom sharing a triangular face with a tricapped trigonal prism of fod oxygens around the europium atom.[25] As expected from the physical measurements, the geometry of the $Co(acac)_3$ species is little changed by the sharing of three oxygens with the europium atom.

Temperature Dependence of Spectra. Although the bound chemical shifts for the adducts are largely insensitive to change in concentration, they are quite sensitive to change in temperature. The $Eu(fod)_3$-induced shifts for the present systems

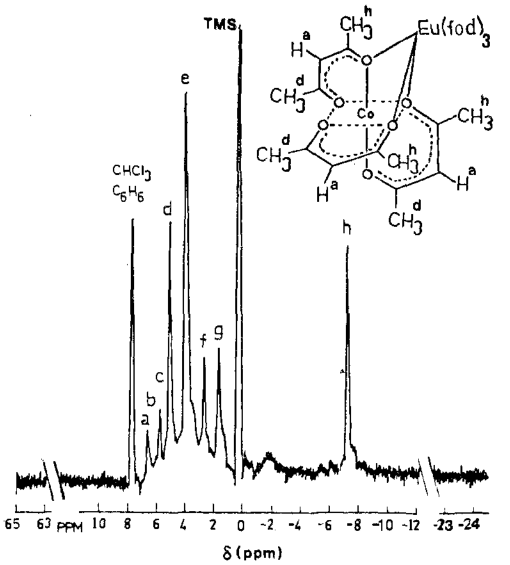


Figure 2. Wide sweep NMR spectrum of $Co(acac)_3$-$Eu(fod)_3 \cdot \frac{1}{2}C_6H_6$ in $CDCl_3$. a, -CH= of adduct (acac); b, -CH= of uncomplexed $Co(acac)_3$; c, -CH= of adduct (fod); d, CH_3 of adduct (acac); e, *t*-Bu of adduct (fod); f, CH_3 of uncomplexed $Co(acac)_3$; g, *t*-Bu of uncomplexed $Eu(fod)_3$; h, CH_3 of adduct (acac).

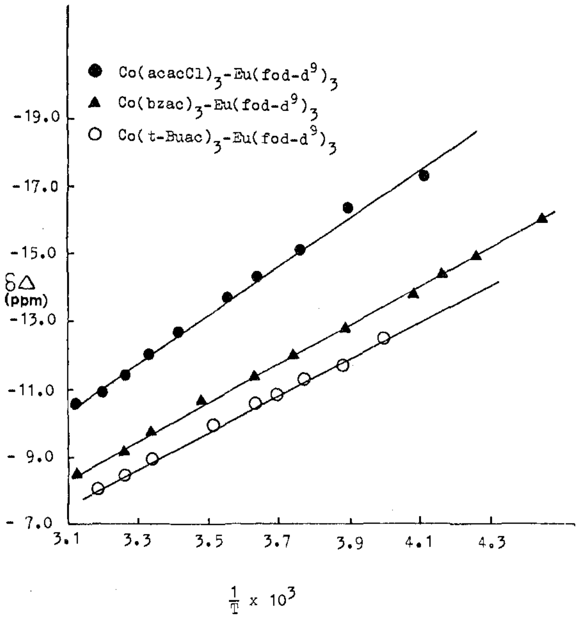


Figure 3. Dependence of lanthanide-induced shifts (δΔ) on temperature; for each adduct the data above correspond to the NMR signal of the CH_3 groups which are adjacent to the site of coordination with $Eu(fod\text{-}d_9)_3$.

are found to follow an approximate linear dependence on T^{-1} as observed by other workers[26] for organic substrates interacting with europium LSR (Figure 3).[27] Figure 4 gives a plot of the lanthanide-induced shifts against T^{-1} for $Co(acacCl)_3$ in equilibrium with its adduct. Lanthanide-induced shifts of both methyl resonances for complexed $Co(acacCl)_3$ show linear dependence on T^{-1} over the range studied and the positions of both methyl signals move toward the position of the uncomplexed methyl signal as the temperature is increased. This decrease in the induced shifts is accompanied by significant line broadening which suggests that an increase in the exchange rate between adduct and substrate also occurs.

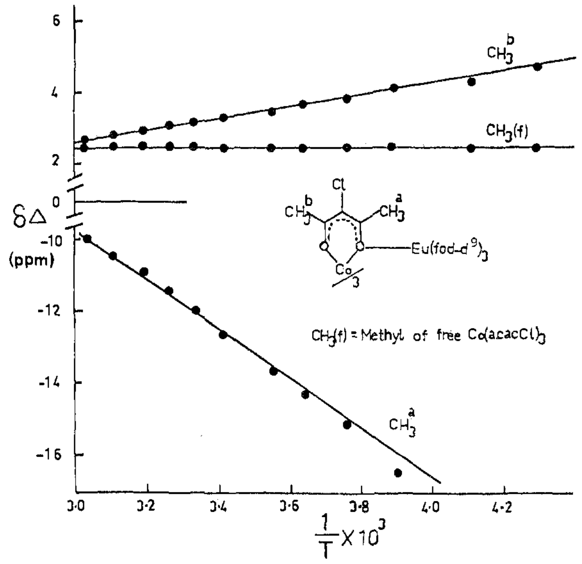


Figure 4. Dependence of lanthanide-induced shifts (δΔ) on absolute temperature for $Co(acacCl)_3$-$Eu(fod\text{-}d_9)_3$ and $Co(acacCl)_3$.

Table III. Equilibrium Constants for $Eu(fod\text{-}d_9)_3$ Adducts Measured at 33 °C

substrate	K,[a] M^{-1}	substrate	K,[a] M^{-1}
Co(*t*-Buac)$_3$	830 ± 300[b]	Co(acacCl)$_3$	240 ± 40
Co(acac)$_3$	820 ± 300	Co(acacBr)$_3$	110 ± 20
Co(bzac)$_3$	530 ± 150		

[a] A duplicate set of values was obtained using $Eu(fod)_3$ rather than $Eu(fod\text{-}d_9)_3$; although affected in some cases by errors resulting from overlap of the *tert*-butyl peak with other signals, the values obtained were in general agreement with those listed above. [b] Assessed errors.

Formation Constants for Adduct Formation. In each spectrum where signals for both the adduct and free substrate are clearly visible, the ratio of the total intensity of the methyl signals in the adduct to the intensity of the methyl signal in the free substrate was measured. Calculations using data from five different concentrations ranging from molar ratios [$Eu(fod\text{-}d_9)_3$:substrate] of 0.1 to 0.8 were performed. From the relative intensities and the total concentration of substrate in solution, the concentration of both the adduct and the free substrate remaining in solution can be obtained. The concentration of free $Eu(fod\text{-}d_9)_3$ in solution [that is, the concentration of added $Eu(fod\text{-}d_9)_3$ which is not coordinated to substrate] was calculated by subtracting the experimentally found concentration for the adduct from the total concentration of $Eu(fod\text{-}d_9)_3$ added. Equilibrium (concentration) constants were obtained for a 1:1 adduct using $K = [LS]/[L][S]$; the values are listed in Table III.

Because of the experimental limitations of the method used in their determination, the K values (Table III) are not of high accuracy. This is especially so for adducts of the substrates $Co(acac)_3$, $Co(t\text{-}Buac)_3$, and $Co(bzac)_3$ where K values are high. For each of these, a small variation in the relative ratio of the resonance signals of the adduct to those of the free substrate can cause a large variation in the calculated K value. Nevertheless, the K values do indicate the approximate order of adduct stability with $Eu(fod\text{-}d_9)_3$. For the five adducts studied the order is

$$Co(t\text{-}Buac)_3 > Co(acac)_3 > Co(bzac)_3 > Co(acacCl)_3 > Co(acacBr)_3$$

If we ignore entropy effects which are difficult to predict, it might be expected that the cobalt complex of any β-diketone which is a weaker Lewis base than acetylacetone would be

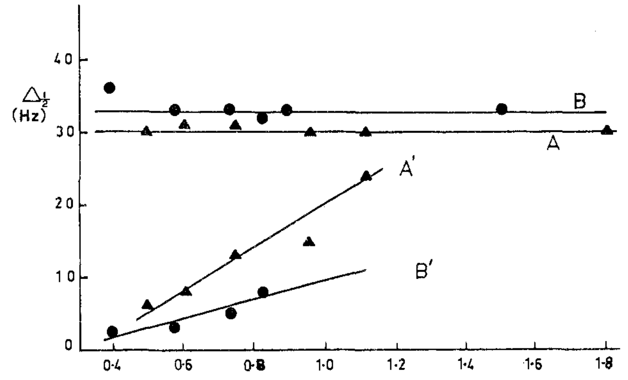


Figure 5. Dependence of line widths ($\Delta_{1/2}$) on Eu(fod-d_9)$_3$ concentration; the data correspond to the NMR signals for the CH_3 groups which are adjacent to the site of coordination with Eu(fod-d_9)$_3$. Temperature = 33 °C. ▲ = $\Delta_{1/2}$ for CH_3 resonance of Co(acacCl)$_3$; ● = $\Delta_{1/2}$ CH_3 resonance of Co(t-Buac)$_3$. A, B, plots for adducts; A′, B′; for free substrates.

coordinated more weakly to Eu(fod-d_9)$_3$ and hence give a lower K value. The presence of electron-withdrawing aryl, chloro, and bromo groups will tend to make Co(bzac)$_3$, Co(acacCl)$_3$, and Co(acacBr)$_3$ weaker Lewis bases than Co(acac)$_3$ toward Eu(fod-d_9)$_3$. Hence the corresponding K values should be lower and this is found experimentally.[28]

The lanthanide-induced bound chemical shifts of the methyl protons adjacent to the europium in the adducts are found to follow a similar order to that observed for the stability constants (Table II). Since the electronic effects just discussed will vary systematically in the order listed, it is perhaps not surprising that the lanthanide-induced shifts also vary in a similar manner; the shifts will be sensitive to any change in geometry of the adduct (if a pseudocontact mechanism is operating) as well as to the degree of covalency in the oxygen–europium bonds (if a contact mechanism is operating). It is noted that the induced shifts get larger as the K values decrease.

Kinetics and Mechanism of Adduct Formation. The two most likely mechanisms involved in exchange for 1:1 adduct formation are the associative mechanism:[29,30]

$$\text{LS} \xrightarrow{\text{slow}} \text{LSL}^* \xrightarrow{\text{fast}} {}^*\text{LS} + \text{L}$$

and the dissociative mechanism:

$$\text{LS} \xrightarrow{\text{slow}} \text{L} + \text{S} \xrightarrow[\text{L}^*]{\text{fast}} {}^*\text{LS} + \text{L}$$

It is possible to differentiate between these mechanisms by study of the line widths of the adduct resonances as a function of the Eu(fod-d_9)$_3$ concentrations.[29,30] Figure 5 illustrates typical plots of line widths at half height of adduct resonances ($\Delta_{1/2c}$) vs. the molar ratio of Eu(fod-d_9)$_3$ to substrate; the effect on the resonances of the methyl groups which are adjacent to the donor oxygen atoms for two different adducts are shown.

The line widths of these adduct resonances are independent of Eu(fod-d_9)$_3$ concentration whereas the line widths of the free substrate resonances increase with added Eu(fod-d_9)$_3$.

The mean lifetime of the adduct (τ_c) in a slow exchange process is related to the line width at half height ($\Delta_{1/2c}$) by[14,31]

$$\frac{1}{\tau_c} = \pi(\Delta_{1/2c} - \Delta^0{}_{1/2c})$$

where $\Delta^0{}_{1/2c}$ is the line width at half height in the absence of exchange.

For a dissociative mechanism, where rate = k_r[LS], it can be shown that[14,30,31]

$$\frac{1}{\tau_f} = k_r \frac{[\text{LS}]}{[\text{S}]}$$

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

where τ_f = mean lifetime of free substrate, τ_c = mean lifetime of adduct, and k_r = first-order reaction rate constant. Since $\tau_f{}^{-1}$ is dependent on the ratio [LS]/[S], the line width of a peak from the free substrate will increase as the concentration of adduct present increases whereas $\tau_c{}^{-1}$ is independent of concentration. This is as found (see Figure 5) and hence the present systems very likely have the unimolecular dissociation of the adduct into substrate and free shift reagent as the rate-determining step.[32,33] In contrast, if an associative mechanism were operating, then a dependence of $\tau_c{}^{-1}$ on LSR concentration would be expected.

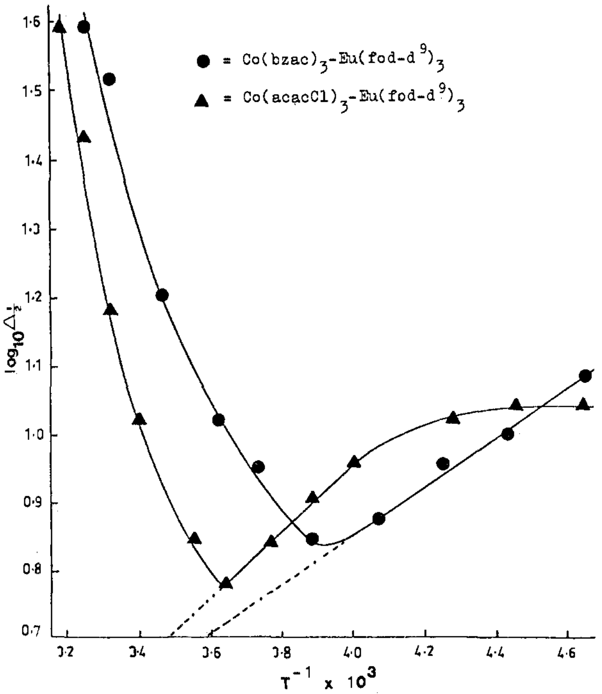


Figure 6. Dependence of line width ($\Delta_{1/2}$) on temperature; for each adduct the data above correspond to the NMR signal of the CH_3 groups which are adjacent to the site of coordination with Eu(fod-d_9)$_3$. Data for 1:1 adduct in $CDCl_3$.

Co(acacCl)$_3$ and Co(bzac)$_3$ were chosen for detailed kinetic study since, for these, both reacting species (adduct and substrate) are very soluble in $CDCl_3$; this enabled each study to be extended to low temperatures [Co(acac)$_3$ and Co(t-Buac)$_3$ crystallized from solution as the temperature was lowered]. Spectra of Co(acacCl)$_3$ plus Eu(fod-d_9)$_3$ in $CDCl_3$ were obtained at a series of temperatures between −60 and 40 °C and the respective line widths at half height were accurately determined. A similar set of spectra were obtained for Co(bzac)$_3$. The signals studied for the Co(acacCl)$_3$–Eu(fod-d_9)$_3$ system were each of the methyl signals of the adduct whereas, for the Co(bzac)$_3$ system, the single adduct methyl signal was used. For temperatures below 33 °C, the line widths in both systems can be measured quite accurately, but at temperatures above this, line broadening becomes much larger and the measurements become less accurate. Plots of log $\Delta_{1/2}$ against T^{-1} are shown in Figure 6.

For Co(acacCl)$_3$–Eu(fod-d_9)$_3$ at temperatures below about 1 °C, where chemical exchange between adduct and substrate is virtually nonexistent, line widths increase with decreasing temperature.[34] Above 1 °C, line widths again increase owing

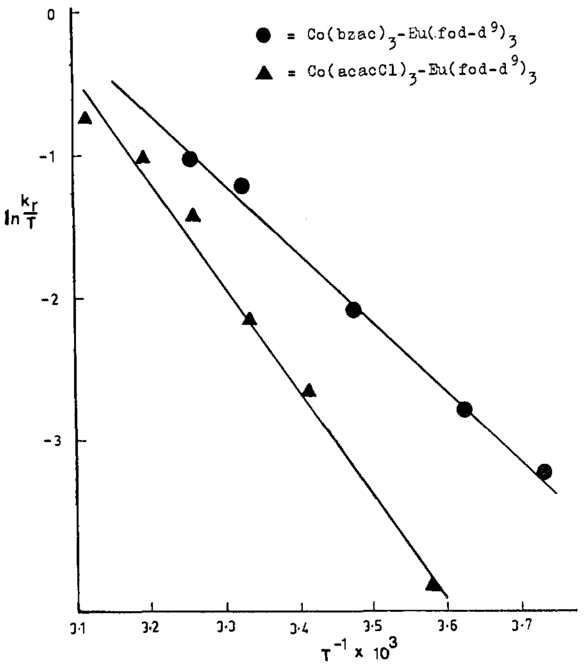


Figure 7. Plots of $\ln k_r/T$ against $T^{-1} \times 10^3$ for the adduct-substrate exchange reactions; for each adduct the data above correspond to the CH_3 groups which are adjacent to the site of binding with Eu(fod-d_9)$_3$.

Table IV. Change of Mean Lifetime (τ_c)^a of Adduct with Temperature

Co(acacCl)$_3$-Eu(fod-d_9)$_3$			Co(bzac)$_3$-Eu(fod-d_9)$_3$		
T, K	k_r, s^{-1} ^{b}	τ_c, s	T, K	k_r, s^{-1} ^{b}	τ_c, s
329	198	5.05×10^{-3}	306	111	9.04×10^{-3}
322	150	6.66×10^{-3}	300	91.0	1.10×10^{-2}
313	111	8.97×10^{-3}	287	35.9	2.79×10^{-2}
306	72.9	1.37×10^{-2}	275	16.7	5.97×10^{-2}
300	34.1	2.93×10^{-2}	267	10.5	9.54×10^{-2}
293	20.0	5.01×10^{-2}			

^{a} Data apply to the CH_3 groups adjacent to the site of binding with Eu(fod-d_9)$_3$. ^{b} $k_r = \tau_c^{-1}$ = first-order reaction rate constant.

Table V. Activation Parameters, Calculated from the Temperature Dependence of the Line Widths of the Methyl Signals for the Adduct Systems Listed

	Co(acacCl)$_3$ + Eu(fod-d_9)$_3$	
	CH_3^{a}	CH_3^{b}
$\Delta H^\ddagger$, kJ mol^{-1}	62 ± 4^c	60 ± 6
$\Delta S^\ddagger$, J K^{-1} mol^{-1}	−8 ± 4	−14 ± 4
	Co(bzac)$_3$ + Eu(fod-d_9)$_3$	
		CH_3^{a}
$\Delta H^\ddagger$, kJ mol^{-1}		40 ± 3
$\Delta S^\ddagger$, J K^{-1} mol^{-1}		−74 ± 11

^{a} CH_3 adjacent to site of attachment of LSR. ^{b} CH_3 groups not adjacent to site of attachment of LSR; owing to the inability to obtain data at greater than 33 °C for this signal [overlap with the -CH= signal of Eu(fod-d_9)$_3$ occurs], this data is of lower accuracy than that derived from the adjacent methyl groups. ^{c} Assessed error.

to exchange broadening dominating the normal expected decrease in line width. Parallel behavior was observed for the adduct of Co(bzac)$_3$ (Figure 6).

Extrapolation to higher temperatures of the linear low-temperature sections of these plots allows determination of $\Delta^0_{1/2c}$ at higher temperatures and hence from $\tau_c^{-1} = \pi(\Delta_{1/2c} - \Delta^0_{1/2c})$ the mean lifetime (τ_c) of the adduct at a particular temperature can be determined.

The τ_c values obtained over a range of temperatures are tabulated in Table IV together with the corresponding first-order rate constants (k_r). The rate of exchange between adduct and free substrate increases with the temperature but, for both systems, chemical exchange remains relatively slow at these elevated temperatures. Even though line broadening is considerably increased, resonances of both adduct and free substrate are still observed at these higher temperatures.

Activation parameters for the dissociation reaction were determined using the Eyring equation; plots of $\ln k_r/T$ vs. T^{-1} are shown in Figure 7. The values of $\Delta S^\ddagger$ and $\Delta H^\ddagger$ were obtained from the intercept and the slope, respectively. A duplicate set of activation parameters derived from the two different methyl signals of Co(acacCl)$_3$-Eu(fod-d_9)$_3$ is listed in Table V. The agreement between the two sets of values is reasonable considering the errors inherent in the experimental procedure. Activation parameters for Co(bzac)$_3$-Eu(fod-d_9)$_3$ are also listed in Table V. It is difficult to assign individual values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ to identifiable molecular processes. However, the positive enthalpy terms are probably associated with the breaking of three europium-oxygen bonds which could dominate the various heat terms. The negative entropy terms may include a contribution from increased solvation on formation of the activated complex but it is not possible to assess the nature of such changes here.

Concluding Remarks

The results presented above again[4,6] demonstrate that LSRs interact with suitable classes of coordination complexes such that adduct formation occurs. The unusual, slow chemical exchange (at ambient temperatures) described for the present systems reinforces our previous observation[6] that, for comparable substrates, the lifetime of an LSR adduct can depend upon the number of binding sites to the LSR. For example, the lifetime ($\tau_c = 1.4 \times 10^{-2}$ s) of the adduct of Eu(fod-d_9)$_3$ with Co(acacCl)$_3$ at ambient probe temperature is approximately 600-fold longer than the value obtained previously[6] for the adduct of type II where fast chemical exchange occurred (and where a lifetime of 2.3×10^{-5} s was observed). Indeed, this latter value is longer than generally observed for simple organic substrates in which there is only one site of attachment to the LSR.[7]

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(19) Assuming that slow exchange is ineffective in averaging the different environments of these methyl resonances.

(20) A possible reason for the absence of 2:1 adduct formation is that, on forming a 1:1 adduct, the delocalized electron density of the β-diketone chelate ring is drawn toward the attached Eu(fod)$_3$. Hence the Lewis basicity of the three oxygens at the opposite end of the Co(acac)$_3$ molecule would be lowered such that their tendency to coordinate to a second Eu(fod)$_3$ is reduced.

(21) In all cases duplicate runs using nondeuterated Eu(fod)$_3$ were made and the results obtained substantiate those obtained with Eu(fod-d_9)$_3$. Similarly a duplicate set of spectral studies using C_6D_6 as solvent were carried out for each of the systems discussed. In each case the C_6D_6 spectra were in qualitative agreement with the analogous spectra using $CDCl_3$ as solvent.

(22) The amount of benzene was in each case calculated from the elemental analysis and was also obtained from accurate integration of the NMR spectra of the adduct dissolved in $CDCl_3$. The benzene is strongly held since it is not removed by heating the compounds at 100 °C in vacuo for 12 h. It is not uncommon for clathrated solvent molecules to be held strongly in the host metal complex structure; see L. F. Lindoy, S. E. Livingstone, T. N. Lockyer, and N. C. Stephenson, *Aust. J. Chem.*, **19**, 1165 (1966).

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(28) It is noted that the halogen-substituted complexes nevertheless show the reverse order to that expected from the relative electronegativities of the substituent halogens. The electronic effects discussed should largely contribute to the enthalpy term for each equilibrium. Since related entropic considerations are far less predictable, these could be the source of the minor irregularity observed for the chloro- and bromo-containing adducts. Alternatively the variation may arise from subtle effects arising from different steric properties of the complexes.

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(32) Nevertheless an alternate mechanism involving substrate displacement by solvent attack, such as

$$\text{LS} + \text{solvent} \rightarrow \text{solvent-LS} \rightarrow \text{solvent-L} + \text{S},$$

cannot be ruled out. Further, it is not possible to distinguish a dissociative mechanism involving a lowering of coordination number of the europium(III) or one in which the coordination number is maintained by substituting solvent molecules.

(33) A related series of preliminary studies involving Pr(fod-d_9)$_3$ has also been performed. In the investigation of Co(β-diketonato)$_3$ complexes with Pr(fod-d_9)$_3$, slow chemical exchange was again observed as indicated by the presence of both adduct and free substrate NMR signals. Similar experiments to those carried out for the Eu(fod)$_3$ systems confirmed that 1:1 adduct formation occurred. As expected for Pr(fod)$_3$, the directions of the lanthanide-induced shifts are opposite in sign to those obtained for the europium LSR. Preliminary experiments concerned with deciding the nature of the slow exchange mechanism indicated that the details are more complicated than for Eu(fod)$_3$ exchange and no detailed analysis was attempted.

(34) For this adduct, a saturation point is reached at −40 °C after which no change in line width is observed. The reason for this behavior is uncertain.

Oxidation–Reduction Reactions of Complexes with Macrocyclic Ligands. Halide-Mediated Electron Transfer Involving Low-Spin Cobalt(III)–(II) Couples[1]

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Abstract: Coordination complex oxidants containing coordinated chloride and bromide react with low-spin $Co^{II}(N_4)(OH_2)_2^{2+}$ substrates (N_4 a tetraaza macrocyclic ligand) at rates about 10^6 times faster than with reagents constrained to react through outer-sphere pathways. Chloride transfer has been demonstrated in "exchange-like" reactions with $Co(N_4)(OH_2)Cl^{2+}$ oxidants. As expected of rate patterns for systems exhibiting weak coupling between metal centers, the halide-bridged inner-sphere reactions vary in their rates over several orders of magnitude. The rate constants are dependent on the free energy of reaction and on intrinsic reorganizational parameters. A series of reactions of the type $Co(N_4)(OH_2)Cl^{2+} + Co(N_4')(OH_2)_2^{2+} \rightleftarrows Co(N_4)(OH_2)_2^{2+} + Co(N_4')(OH_2)Cl^{2+}$ has been investigated in which the low-spin cobalt(II) complexes are known to differ in their axial, Co–OH_2 bond lengths, and for which this structural difference is known to be directly reflected in a several orders of magnitude range of outer-sphere $Co(N_4)(OH_2)_2^{3+,2+}$ electron transfer rate constants. With reference to this series of reactions the 10^6-fold rate advantage of the Cl^--bridged inner-sphere pathway has been shown to arise from (1) a much smaller reorganizational term associated with first coordination sphere bond length changes (50% of λ_i for the outer-sphere pathway); (2) a reduction of the solvent reorganizational term (λ_o) to nearly zero; and (3) possibly a small contribution (of the order of a factor of 30 in the rate constant) due to the greater adiabaticity of the inner-sphere reactions. For sufficiently powerful oxidants, the inner-sphere rates approach a limiting value, one or two orders of magnitude smaller than the diffusional limit, consistent with rate-determining substitution on the low-spin $Co(N_4)(OH_2)_2^{2+}$ complex ($k_w \sim 10^9\ s^{-1}$).

Introduction

At the present stage of maturity in the study of electron transfer reactions there is general agreement on many of the gross features which determine patterns of reactivity.[2] However, the limits of theoretical descriptions have not always been well substantiated by experimental evidence, and in some kinds of system it is not clear what kind of theoretical model is applicable. Thus those electron transfer reactions in which a

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