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NUCLEAR MAGNETIC RESONANCE STUDIES OF COORDINATION METAL COMPLEXES USING LANTHANIDE SHIFT REAGENTS

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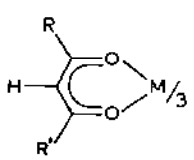
CONTENTS

A. INTRODUCTION

Lanthanide shift reagents (LSRs) such as **1** and **2** have been used routinely



LSR abbreviation

1 R = *t*-Bu; R' = *t*-Bu — M [dpm]$_3$
2 R = *t*-Bu; R' = C_3F_7 — M [fod]$_3$

to simplify the NMR spectra of organic compounds containing suitable heteroatoms [1,2]. The lanthanide ions in these reagents can readily expand their coordination number to seven, eight or nine by binding to the heteroatoms of one or more molecules of the substrate under study. The interac-

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tion between the paramagnetic lanthanide ion and the nuclei of the substrate causes alteration of the magnetic environment of each nucleus and changes in the corresponding NMR chemical shifts result. Apart from tris-chelated reagents of which **1** and **2** are typical, free trivalent lanthanide ions (in polar solvents) have also found limited use as shift reagents.

Although LSRs have been employed for both structural assignment and conformational analysis of a range of organometallic compounds [3], similar NMR studies involving classical coordination complexes have been much less common. Nevertheless the studies so far completed indicate that, for suitable complex types containing available Lewis base sites, LSR studies can be quite informative and yield information which may be difficult to obtain by other techniques. Both stereochemical studies using LSRs and a limited number of investigations concerned with kinetic and thermodynamic aspects of the LSR–metal complex have been reported. The aim of the discussion which follows is to illustrate the scope of these studies and to provide a useful foundation for future research in this little studied area.

B. LSR INTERACTION AT NON-DONOR SITES

Examples in which the LSR interaction occurs at non-donor sites of the substrate complex under study have been documented. For example, $Eu(fod)_3$ has been used to distinguish between N-bonded and S-bonded thiocyanato ligands in a range of mixed-ligand metal complexes in $CDCl_3$ [4]. The LSR binds to the uncoordinated nitrogen atom when the thiocyanate is S-bonded to the metal ion and in these cases shifts in the proton resonances of suitable attached organic ligands are observed. As is usual with LSRs, the equilibrium between adduct and free substrate is rapid on the NMR time scale giving rise to a time-averaged spectrum in each case. When the thiocyanate is N-bonded, no significant interaction occurs. This ability of the LSR to coordinate to nitrogen rather than sulfur reflects the 'hardness' of Eu(III). The procedure thus provides a convenient method for deciding the bonding mode in thiocyanato complexes and hence also for distinguishing linkage isomers in such complexes when they occur.

Europium(III) perchlorate in aqueous solution has been used as an LSR to aid assignment of the methyl resonances arising from the disulfide complex shown in Fig. 1 [5]. The methyl resonances occur as an overlapping three peak pattern in the absence of LSR (Fig. 1a). Addition of europium ion to an aqueous solution of the complex leads to shifts in the methyl resonances as shown in Fig. 1b. The Eu(III) binds to an oxygen of the pendant acetate group such that the methyl signals arising from this group are preferentially shifted upfield relative to those attached to the corresponding chelated moiety and clear signal separation occurs.

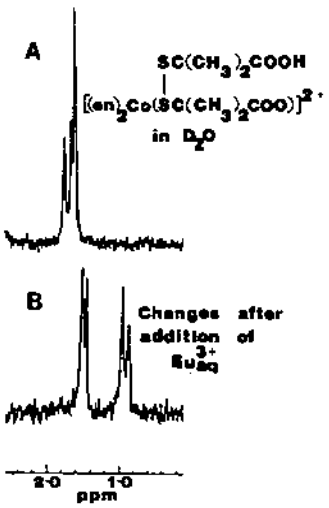
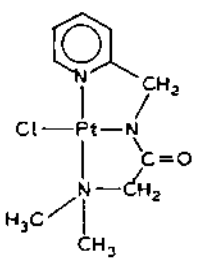


Fig. 1. (A) The methyl multiplet in the NMR spectrum of the cobalt complex. (B) The separation of the methyl signals after addition of excess europium perchlorate.

A further example in which the LSR appears to interact with a heteroatom site which is remote from the site of binding of the ligand to the central metal of the complex is given by the interaction of $Eu(dpm)_3$ with the square-planar complex **3** [6]. The induced shifts observed for the proton



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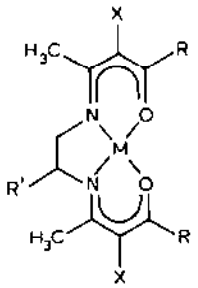
resonances of the organic ligand presumably result from interaction of the LSR with the non-coordinated acetocarbonyl group although the possibility that attack occurs at the electron lone pair of the coordinated amido group cannot be discounted. This latter type of interaction in which a coordinated heteroatom of the substrate simultaneously binds to the LSR has been shown to occur in other systems. Some examples of this type are discussed below.

C. LSR INTERACTION VIA DONOR ATOM BRIDGE FORMATION

In an early study, the effect on the NMR spectrum of $CH_3Co(salen)H_2O$ (where salen = *N*,*N*′-ethylenebis(salicylideneiminato)) in deuterated di-

methyl formamide on addition of lanthanide salts was investigated [7]. In contrast to the effects of paramagnetic transition metal ions for which the shifted peaks were extensively contact broadened, the hydrated nitrates of Pr(III), Nd(III) and Sm(III) result in only weak broadening. With Tb(III), Ho(III) and Yb(III) similar results were obtained although both shifts and broadening effects were greater with these ions. Since salen complexes have been well documented to form adducts with a range of metal salts via bridge formation involving the oxygens of the coordinated ligand [8], a similar bridged structure for the respective LSR adducts was assumed in this study.

A comprehensive study of the interaction of $M(fod)_3$ (M = Eu, Pr) with diamagnetic metal complexes of type **4** is also complete [9]. A range of appropriately substituted square-planar complexes of this type are readily synthesised. Such complexes have the necessary solubility in $CDCl_3$ and are able to interact with LSRs such as **1** or **2** via the lone-pair electron density of the *cis* oxygen donors to yield 1 : 1 adducts (such as **5**) in an analogous



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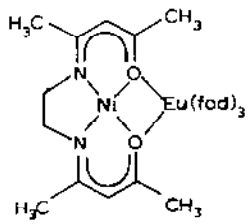
M = Ni, Pd, Pt
R = alkyl group
R' = H or CH_3
X = H, Cl, Br, I, CH_3, SC_6H_5



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manner to that proposed above for the Co(III) salen complex. However, in the present adducts the europium ion may be out of the donor plane of the substrate complex [10]. Related adducts of the parent complex type in which bridge formation occurs to a transition metal ion such as copper [8] or to an alkali metal ion such as sodium [11] have been documented previously; the latter adduct type is of particular relevance since the oxygen—sodium bonds will be essentially electrostatic and thus similar to the bond type normally postulated to occur between LSRs and organic substrates [2]. Such adduct formation is also qualitatively similar to the weak self-association via bridging oxygen atoms shown to occur for $Eu(fod)_3$ in CCl_4 [12].

Incremental addition of $Eu(fod)_3$ to a $CDCl_3$ solution of the parent nickel complex (**4**; R = CH_3; X, R' = H) results in the induced shifts illustrated in Fig. 2 (broadening of certain signals was also observed; the kinetic implications are discussed later in this review) [9]. Clearly, 1 : 1 adduct formation occurs and from the shape of the curves a binding constant, K, of ca. 10^3 M^{-1} can be estimated for the equilibrium: complex + LSR $\rightleftharpoons$ complex–LSR. A related experiment in which $Pr(fod)_3$ was substituted for $Eu(fod)_3$ led to a

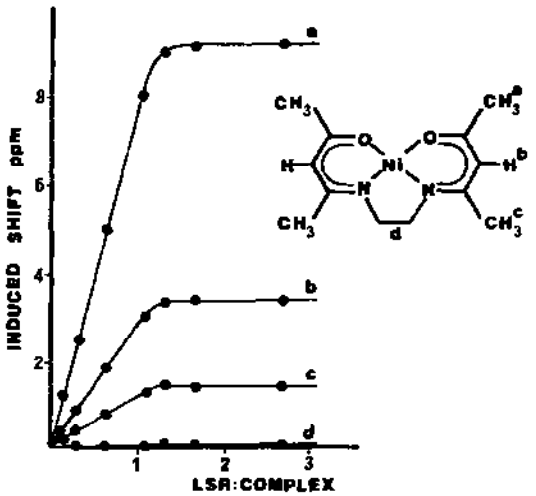


Fig. 2. The lanthanide-induced shifts induced by $Eu(fod)_3$ in the ^1H NMR spectrum of **4** (M = Ni, R = CH_3, R' = H, X = H).

similar shift pattern except that, as is usually the case with this LSR, most shifts were to high field. In both these cases, a general trend of diminution of the absolute magnitude of the induced shift with distance of the respective protons from the LSR was observed. Nevertheless, attempts to fit the observed pattern using the McConnell–Robertson equation [13], which can be used to predict induced shifts if only a pseudo-contact (through space) mechanism is operating, were unsuccessful. For axially symmetric systems, the pseudo-contact shift of nucleus i, Δ_i, is given by $\Delta_i = K(3\cos^2\theta_i - 1)/r_i^3$ where r_i is the distance from the lanthanide to nucleus i and θ_i is the angle between the nucleus–lanthanide vector and the principal magnetic axis of the lanthanide (usually assumed to be colinear with the LSR–substrate bond for substrates having a single binding site). Thus in the case of a pseudo-contact mechanism, the magnitude of an induced shift will depend solely on the position in space of the substrate metal complex with respect to the LSR. However, a comparison of the relative induced shifts of corresponding protons for the complexes of type **4** (with R = CH_3 and X = H, Cl, Br, I, CH_3, SC_6H_5) indicates considerable variation along this series even though the overall geometry of the substrate complex would not be expected to alter significantly on variation of the substituent X. This, together with an observed alteration of sign of the observed shifts corresponding to the conjugated carbon backbones of the ligand in the ^{13}C NMR spectrum, strongly suggests that a contact (through-bond) shifting mechanism is also significant in these systems. Although the absolute magnitude of such a

contribution normally diminishes along a carbon chain as the number of covalent bonds linking successive carbons to the LSR increases, the sign of the contact term is expected to alternate along such a chain [2]. The presence of a contact term (which implies that there is some covalency in the Eu–O bonds) may thus explain the inability to fit the observed shifts to the McConnell–Robertson equation. By choice of appropriately substituted (nickel) complexes of type **4**, it has been possible to demonstrate the influence of both steric and electronic effects on the lanthanide induced shifts [9]; for example, when R is a bulky alkyl group (such as tert-butyl), adduct formation is inhibited due to steric blocking of the approach of the LSR and no lanthanide induced shifts are observed. As the size of R is reduced, adduct formation again occurs but in each case the binding constant is lower than for the complexes with $R = CH_3$. Similarly when R is an electron-withdrawing group (such as CF_3), the Lewis basicity of the donor oxygen atoms is reduced and no adduct formation occurs. It is significant that the analogue of **4** ($R = CH_3$; R′, X = H) in which the oxygens have been replaced by sulfur donors also gives no adduct formation with $Eu(fod)_3$ or $Eu(dpm)_3$. This is undoubtedly a consequence of the lower affinity of the 'soft' sulfur atoms for Eu(III) [14].

D. A CONFORMATIONAL STUDY USING LSR

The technique has formed the basis for a conformational study of the backbone derived from propylenediamine in **4** (M = Ni; R,R′ = CH_3; X = H) [9]. At 100 MHz, the spectrum of this portion of the molecule consists of a largely second-order set of overlapping resonances in the region 2.5–4.0 ppm. Addition of $Eu(fod)_3$ to the complex in $CDCl_3$ leads to shifts in the respective resonances. When a LSR : complex ratio of 0.3 had been reached, a first-order pattern consisting of a five peak multiplet, a four peak multiplet and a doublet was present. This pattern corresponds to the first-order coupling scheme shown in Fig. 3. In this scheme it is assumed that the coupling constant between H_f and H_d is zero as predicted by the Karplus relationship [15] when the dihedral angle between these protons is 90°. From the LSR shifted spectrum, the individual coupling constants were measured directly. The chemical shifts of the resonances in the initial spectrum were estimated by extrapolation of the appropriate chemical shifts in the expanded spectra to values at zero concentration of $Eu(fod)_3$. Using these chemical shifts and the coupling constants obtained from the shifted spectra, the original overlapping spectrum was successfully simulated with the aid of the LAOCN III computer program. The excellent agreement obtained between the experimental and simulated spectra provides strong evidence that the first-order coupling scheme outlined in Fig. 3 is correct. In addition, the

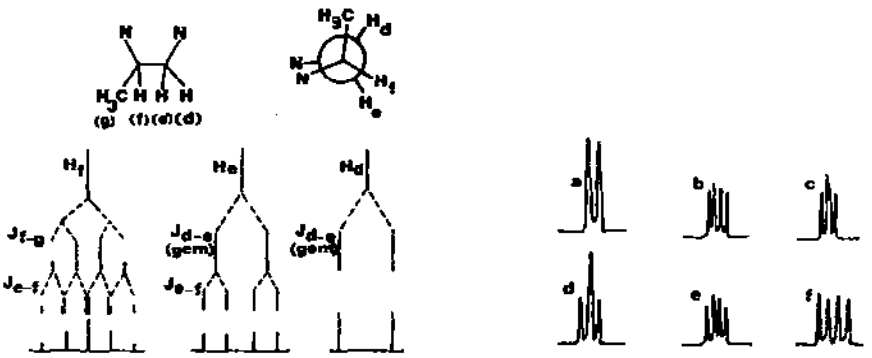


Fig. 3. First-order NMR coupling scheme for the propylenediamine backbone of **4** (M = Ni, R = CH_3, R′ = CH_3, X = H).

Fig. 4. Changes in the propylenediamine methyl resonance of a racemic mixture of **4** (M = Ni, R = CH_3, R′ = CH_3, X = H) on addition of Eu[(+)fpc]$_3$: a, original methyl doublet; b–f, changes on addition of LSR.

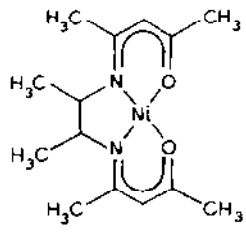
assignments agree with those from a previous NMR study of this complex using the INDOR technique [16]. An important consequence of these assignments is that the conformation of the chelate ring derived from propylenediamine must be such that the methyl group occupies an axial position. X-ray diffraction has shown this to be the case for the corresponding Cu(II) complex of this ligand [17].

E. CHIRAL STUDIES USING OPTICALLY ACTIVE LSR

In the presence of a chiral LSR, such as (+)tris[3-heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III), Eu[(+)fpc]$_3$, the two enantiomers of **4** (M = Ni; R, R′ = CH_3; X = H) resulting from the presence of the asymmetric carbon in the propylenediamine backbone would be expected to exhibit different shift behavior since the corresponding LSR adducts are diastereomers. Addition of the above LSR to a racemic mixture of the complex does result in a composite of two overlapping spectra [9]; the changes in the methyl doublets as LSR is added are shown in Fig. 4. Combined with spectral integration, this technique thus provides a useful means for assaying mixtures of suitable optically-active complexes. In the present case, the preparation of the complex containing the R-form of the ligand directly from R-propylenediamine has been carried out and, by means of a comparative LSR study, assignment of the individual resonances to particular isomers has proved possible.

As an extension of the above investigation [9], studies involving the

isomers of **6** derived from the *racemic* and *meso* forms of 2,3-diaminobutane



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have been carried out. With the *racemic* isomer, Eu[(+)fpc]$_3$ yields the expected two sets of resonances resulting from the presence of the R,R- and S,S-diastereomers in solution. With the *meso* form, a doubling of each spectral peak was also observed but, in this case, the doubling is a consequence of the presence of a *meso* plane in the molecule which renders each half of the molecule enantiotropic. The chiral LSR thus affects each half of the molecule differently and two sets of peaks result.

In a related study, addition of Eu[(+)fpc]$_3$ to β-[Ru$_2$(S$_2$CN(CH$_3$)$_2$)$_5$]BF$_4$ in $CDCl_3$ has been used to distinguish the $\Delta\Delta$ and $\lambda\lambda$ stereoisomers of this complex [18]. However, the nature of the LSR–substrate interaction was not delineated in this study.

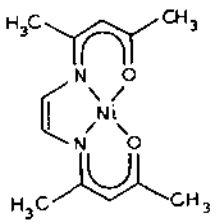
F. SPIN-LATTICE RELAXATION STUDIES USING Gd(fod)$_3$

^{1}H and ^{13}C NMR spin-lattice relaxation rates are significantly reduced in the presence of small amounts of the relaxation reagent, Gd(fod)$_3$. Everett and co-workers [10] have used the paramagnetic contributions to the observed ^{1}H and ^{13}C relaxation rates to locate the position of the bound Gd(III) ion relative to the nuclei of **4** (M = Ni; R = CH_3; R′, X = H) by use of the Solomon–Bloembergen equation [19]. The data are consistent with the binding of Gd(fod)$_3$ to the two oxygens of the metal complex but with the Gd(III) ion being located about 1.8 Å out of the plane of the complex. Steric interactions between the methyl groups of the complex and the fod ligands were proposed to account for the out-of-plane coordination. Subsequent studies [20] involving substitution of Gd(NO$_3$)$_3$ for Gd(fod)$_3$, or **7** for the substrate complex, each gave related results which confirmed the original model of out-of-plane bonding by the Gd(III) reagent.

G. NON-DILUTE FAST EXCHANGE KINETIC STUDIES

Kinetic aspects of the exchange of adducts formed between **4** (M = Ni, Pt; R = CH_3; R′, X = H) and Eu(fod)$_3$ have been investigated [21]. In addition

to the induced chemical shifts already described, addition of $Eu(fod)_3$ to **4** (M = Ni; R = CH_3; R′, X = H) in $CDCl_3$ results in changes in the line-



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widths of the proton resonances. As LSR is added the linewidths at first broaden then narrow; such behavior matches that expected for the little reported non-dilute case of two-site fast-exchange line broadening [22]. From the concentration dependence of the chemical shift and the linewidth, the lifetime of the adduct (and the rate constants for its formation and dissociation) can be determined using [23]

$$\Delta\nu_{1/2} = f_A\Delta\nu_A + f_B\Delta\nu_B + f_A^2 f_B \tau_B^2 \pi\delta^2$$

where $\Delta\nu_{1/2}$ is the half-width of the observed resonance (in Hz) at half-height; $\Delta\nu_A$ is the half-width of the corresponding metal complex resonance in the absence of adduct formation; $\Delta\nu_B$ is the half-width on complete adduct formation; f_A is the mole fraction of free metal complex; f_B is the mole fraction of the metal complex as the LSR adduct; τ_B is the lifetime of the adduct; and δ is the difference in Hz between the original chemical shift and the limiting chemical shift on complete adduct formation.

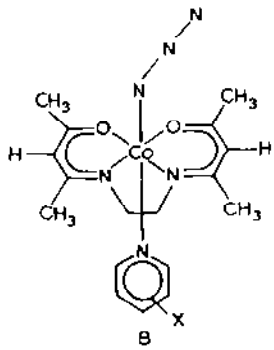
From the linewidth behavior of the resonance corresponding to the methyl groups adjacent to the oxygen donors, a lifetime of 2.3×10^{-5} s was obtained at 32°C for the adduct of **4** (M = Ni; R = CH_3; R′, X = H) and a similar value of 2.2×10^{-5} s was found for the adduct of the analogous Pt(II) complex. The appreciable concentrations of free complex and its LSR adduct during the experiment together with the generally large induced chemical shifts which are a feature of these systems result in the last term of the above expression having a significant influence on the line-broadening behavior. This contrasts with the more commonly observed dilute case for which this term is negligible [24]. Recently similar line-broadening behavior has been observed in the 400 MHz spectra of cholesterol and n-alkanols on the addition of $Eu(dpm)_3$; such broadening is insignificant in the corresponding 100 MHz spectra in which smaller chemical shifts occur [25].

For the exchange process

$$\text{Complex} + \text{LSR} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \text{Complex–LSR}$$

$k_d = \tau_B^{-1}$ and $k_f/k_d = K$. Since the equilibrium constant K could be determined directly from the variation of the induced shift with $Eu(fod)_3$ concentration, this enabled the second order rate constant for adduct formation (k_f) to be calculated also. Values for k_f of ca. 10^7 M^{-1} s^{-1} were obtained for each of the above systems.

In an extension of the above study, the interaction of deuterated $Eu(fod)_3$ with a series of cobalt(III) complexes of type **8** in $CDCl_3$ has been investigated [26]. An X-ray diffraction study on the parent complex (**8**; X = H)



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shows that it has a *trans*-octahedral structure [27] and subsequent NMR studies confirmed that such a structure persists throughout the series [26]. As LSR is added, all resonances in the respective ^1H and ^{13}C NMR spectra shift and it is clear that 1 : 1 adduct formation again occurs in each case. Indeed the 1 : 1 adduct of the parent complex has been crystallized and characterized. The azido asymmetric stretching mode in the IR spectrum of the solid adduct (nujol mull) occurs at 2060 cm^{-1} compared with 2022 cm^{-1} for the free cobalt complex. The increase in frequency on adduct formation suggests that the azido group is involved in bridge formation to the LSR [28]. Strong confirmation that this is also the case in solution was provided by an IR study of the incremental addition of $Eu(fod)_3$ to a solution of the complex in $CDCl_3$. As $Eu(fod)_3$ was added, a decrease in the intensity of the terminal azide stretching mode (at 2024 cm^{-1}) occurred and a concomitant rise of a bridging mode (at 2058 cm^{-1}) was evident. In this study 1 : 1 stoichiometry was also indicated by the disappearance of the bands for the free complex (and the absence of further change in the adduct bands) slightly after a 1 : 1 ratio of LSR to complex had been reached. ^1H NMR studies also confirmed 1 : 1 adduct formation in $CDCl_3$ for all the complexes of type **8**. A model corresponding to attachment of each complex to the LSR via the two oxygens of the tetradentate ligand as well as the terminal nitrogen of the coordinated azido group best fits the available evidence. As in the study discussed previously, the ^{13}C NMR spectrum of **8** (X = H) again gave evidence for a contact contribution to certain of the induced shifts and

no attempt was made to interpret the observed shifts in terms of the McConnell–Robinson equation [13].

For complexes of type **8**, a kinetic study based on the linewidth behavior of the resonance corresponding to the methyl groups adjacent to the nitrogen donors of the tetradentate ligand has been carried out. Lifetimes of between 10^{-3} and 10^{-4} s were observed at 33°C and it is apparent that substituents on the coordinated heterocyclic base have little effect on the lifetime of the adduct. It is perhaps significant that each of these adducts has a longer lifetime than the corresponding adducts of type **4** complexes which bridge only via two oxygens (and for which lifetimes of ca. 10^5 s were observed) [21].

For the study involving **8** (X = H), the variation of linewidth of the methyl resonance with change in LSR concentration is illustrated in Fig. 5; the shape of this curve is also typical of those obtained in the related studies involving complexes of type **4**. In all cases the maximum linewidth occurs when the LSR : complex ratio is ca. 1 : 3. This observation provides additional evidence for the correctness of the analysis since, provided the K value for 1 : 1 adduct formation is large, differentiation of the line-broadening expression leads to the prediction that maximum broadening should occur when the LSR : complex ratio is 0.33.

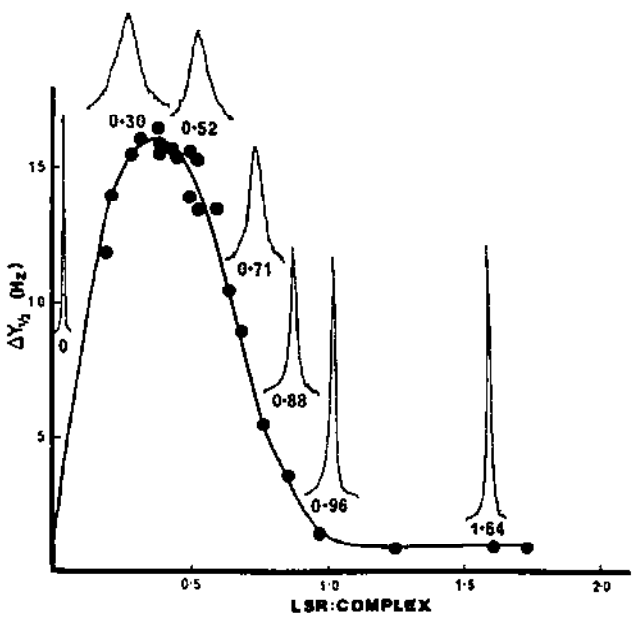
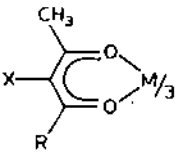


Fig. 5. Changes in the linewidth of the resonance corresponding to the methyl groups adjacent to the imine functions of 4 (M = Ni, R = CH_3, R′ = H, X = H) on addition of Eu(fod)$_3$. $\Delta\nu_{1/2}$ = half width of resonance at half height.

H. SYSTEMS UNDERGOING SLOW EXCHANGE

The interaction of $Eu(fod)_3$ (or its deuterated analogue) with a series of $M(\beta$-diketonato$)_3$ complexes of type **9**, which are potentially capable of



M = Co, Rh
X = H, Cl, Br
R = CH_3, C_6H_5, t-C_4H_9

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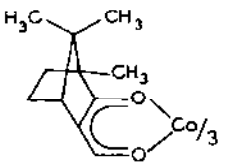
presenting three oxygen donors simultaneously to the LSR, has been studied [29,30]. For the complexes of the unsymmetrical β-diketones, the facial (*cis*) isomers of the respective complexes were used for the LSR studies. Unusual slow LSR exchange with respect to the NMR time scale occurs for the adducts of all these complexes in $CDCl_3$ or C_6D_6. As LSR is added, ^1H NMR signals resulting from free metal complex as well as its adduct with LSR are observed simultaneously at ambient probe temperature. As further LSR is added, the intensity of the original signals decrease and there is a concomitant rise in the intensity of the adduct signals. For example, addition of deuterated $Eu(fod)_3$ to **9** (M = Co, R = CH_3, X = H), $Co(acac)_3$, in $CDCl_3$ results in reduction of the ^1H NMR intensities of the CH_3 and —CH= singlets resulting from the free complex together with the rise of two broad new signals at −6.80 and 4.52 ppm which correspond to the now non-equivalent methyl groups in the adduct [29]. In addition, a new signal at 6.09 ppm was assigned to the —CH= group of the bound cobalt complex. When greater than a 1 : 1 ratio of LSR to cobalt complex is reached, then neither of the original signals remain and no further change in the adduct signals occur. The observed behavior is consistent with the formation of a symmetrical 1 : 1 adduct in which adduct formation occurs along the C_3 axis of the cobalt complex such that three acetylacetonato oxygen atoms, around one face of the octahedron, bridge to the LSR. Parallel ^{13}C NMR studies lead to a similar conclusion [30]. The above adduct has been crystallized and characterized in the solid state [29]. Elemental analyses confirm the 1 : 1 stoichiometry and visible and IR spectral measurements indicate that the coordination sphere of the cobalt complex is little altered on adduct formation. An X-ray diffraction study confirmed the predicted structure [31]; the octahedron of oxygen atoms around the cobalt share a face with a tricapped trigonal prismatic arrangement of oxygens around the europium ion. The adduct exhibits C_3 symmetry.

It is significant that when the cobalt(III) [29] or rhodium(III) [30] complex

of a β-diketone for which both R groups are bulky, such as dibenzoylmethanato (dbm) or dipivaloylmethanato (dpm), was used for similar experiments, no significant interaction with LSR occurred. For these substrates the bulky groups sterically hinder both sets of three oxygens at which adduct formation could take place. The above behavior contrasts with the ready adduct formation which occurs for facial isomers of complexes of unsymmetric β-diketones in which only one face is blocked by bulky R groups and provides further evidence for the validity of the overall model for adduct formation.

In a related investigation the interaction of deuterated Eu(fod)$_3$ with the four diastereomers of Co[(+)hmc]$_3$ (**10**) has been studied [30]. Four di-



Co [(+)hmc]$_2$

10

astereomers occur since the ligand is chiral and the donor oxygens of each ligand are nonequivalent; the diastereomers have been designated *Δ-trans*, *Λ-trans*, *Δ-cis*, and *Λ-cis*, where *Δ* and *Λ* imply right- and left-hand helicity about the C_3 or pseudo-C_3 axis and *cis* and *trans* refer to the relative arrangements of the non-equivalent donor atoms in the coordination sphere. Models suggest that each isomer appears capable of presenting one octahedral face of three oxygens to the LSR in an analogous manner to that discussed for complexes of type **9**. In accord with this, slow chemical exchange was observed for these systems at ambient temperature and 1 : 1 adduct formation was apparent in each case. However, when the ^{1}H and ^{13}C NMR spectra of the respective adducts were monitored against time, it was clear that LSR-induced stereoisomerization occurs. Coordination of LSR to the donor oxygens of Co[(+)hmc]$_3$ will cause a drain of electron density from the corresponding cobalt–oxygen bonds towards the LSR and hence weaken these bonds. As a result, facile rupture of one of these bonds appears possible allowing rearrangement of the adduct via a five-coordinate (with respect to cobalt) intermediate. Alternatively such bond weakening could also facilitate stereoisomerization via the 'trigonal' or 'rhombic' twist mechanisms [32]. From a detailed study of the spectral changes (facilitated by the slow exchange condition), it has proved possible to eliminate certain of the possible mechanisms for stereoisomerization of individual isomers [33].

Since signals for the adduct and the free substrate are observed during the addition of LSR, the strength of adduct binding can be estimated from the relative intensities of the methyl peaks for the bound and free substrate for a given LSR : substrate ratio. For $Co(acac)_3$, a K value of 830 ± 300 M^{-1} was obtained for the adduct with deuterated $Eu(fod)_3$ in $CDCl_3$ at 33°C [29]. As might be expected if entropy effects are assumed not to dominate the interaction, introduction of electron-withdrawing chloro or bromo substituents at X in **9** (M = Co; R = CH_3) led to a reduction of the adduct binding constants and values of 240 ± 40 and 110 ± 20 M^{-1} were obtained, respectively. Substitution of Rh(III) for Co(III) in complexes of type **9** also results in a drop in the corresponding K values [30]: for the adduct of **9** (M = Rh; R = CH_3; X = H) a K value of 26 ± 5 M^{-1} was obtained whereas for **9** (M = Rh; R = CH_3; X = Cl) the value was 4 ± 2 M^{-1}. For the rhodium complexes, X-ray structural data [34] indicate that the donor oxygens will be slightly further separated than in the cobalt analogues [35] and this may be the cause of the observed weaker binding of the Rh(III) complexes to the LSR.

Calorimetric studies involving selected complexes of type Co(β-diketonato)$_3$ have been carried out and enthalpy values as well as formation constants for the respective complexes estimated [36]. In these studies a benzene solution of the cobalt complex was titrated with $Eu(fod)_3$ (in benzene) and the heat changes followed. From the resultant calorimetric titration curve (corrected for heats of solvation) both the K value for adduct formation as well as ΔH^0 for the reaction were obtained. For **9** (M = Co; R = CH_3; X = H), 1 : 1 adduct formation was confirmed and a K value of $> 10^4$ M^{-1} was indicated. The value is higher than that observed for this adduct in the more polar solvent, $CDCl_3$, for which solvation effects will be larger. Parallel ^1H NMR titrations in $CDCl_3$ and C_6D_6 confirmed the above dependence of K value on solvent.

Similar studies were carried out using **9** (M = Co, R = C_6H_5, X = H), $Co(bzac)_3$, and $Co(dbm)_3$; all the results are summarized in Table 1. Approximately zero heat changes were obtained in both of the latter systems and thus, for these, either adduct formation is insignificant or the enthalpy term is near zero. For $Co(dbm)_3$, the approximately zero ΔH^0 value may be attributed to the absence of adduct formation resulting from steric blocking of the donor sites as discussed previously. The corresponding ^1H NMR study confirmed that adduct formation was insignificant in this case. In contrast, a similar ^1H NMR titration experiment clearly indicated that *fac*-$Co(bzac)_3$ undergoes 1 : 1 adduct formation in C_6D_6 with a K value of $\geqslant 10^3$ M^{-1}. Thus adduct formation is entropy controlled in this case and the

TABLE 1

Thermodynamic data for the interaction of $Eu(fod)_3$ with the cobalt(III) complexes of β-diketones

Adduct system	Calorimetry [a]		^1H NMR [b]
	$-\Delta H^0$ (kJ M^{-1})	K (M^{-1})	K (M^{-1})
$[Co(acac)_3]+[Eu(fod)_3]$	30.5 ± 1.2	10^4	$\geqslant 10^4$
$[Co(bzac)_3]+[Eu(fod)_3]$	1 ± 1		$\geqslant 10^3$
$[Co(dbm)_3]+[Eu(fod)_3]$	— [c]		~ 0

[a] In C_6H_6 at 30°C. [b] In C_6D_6 at 33°C. [c] No heat change detected.

negligible ΔH^0 value suggests that the aryl groups are very effective in reducing the Lewis basicity of the three oxygen donors.

J. KINETICS OF SLOW EXCHANGE

The slow exchange observed for the adducts of complexes of type **9** [29] contrasts markedly with previous LSR studies for which chemical exchange has invariably been fast on the NMR time scale when the experiments were performed at ambient temperature [2,3]. However, it has been demonstrated for a few organic substrates that the normally-observed fast exchange can be slowed by lowering the temperature. For example, Evans and Wyatt studied the adduct formed between dimethyl sulfoxide and $Eu(fod)_3$ [37]. At ambient temperature fast exchange was observed. However, at -80°C, two signals (complexed and non-complexed DMSO) were present. By integration of the spectrum, equilibrium constants and solvation numbers for the systems were able to be calculated.

Possible mechanisms for exchange for the present (tris-β-diketonato metal) systems involving 1 : 1 adduct formation are the associative mechanism (rate = k_a[LS][L])

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

and the dissociative mechanism (rate = k_d[LS])

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

From the observed line-width behavior of the adduct and free substrate resonances as the LSR : substrate ratio is varied, it is possible to decide between these mechanisms; a dissociative mechanism was found for each of the present systems.

For slow chemical exchange

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

where k_d is the first-order dissociation rate constant, τ_c is the mean lifetime of the adduct, $\Delta_{1/2c}$ and $\Delta^0_{1/2c}$ are the line widths at half height in the presence and absence of exchange, respectively. The deuterated $Eu(fod)_3$ adducts of $Co(acacCl)_3$, *fac*-$Co(bzac)_3$ and $Rh(acacCl)_3$ gave lifetimes of 1.4×10^{-2} s, 9.0×10^{-3} s, and 6.9×10^{-3} s, respectively. As expected from the observed slow exchange condition, these values are longer than the lifetimes of 10^{-3}–10^{-4} s found for the adducts of complexes of type **8** (bridge formation to the LSR via an O_2N-donor set) and of type **4** (bridge formation to the LSR via an O_2-donor set) for which τ_c values of 10^{-5} s were obtained.

K. CONCLUDING REMARKS

From the above discussion it is clear that, in contrast to the enormous number of LSR studies involving organic substrates now performed [1,38], similar studies involving coordination complexes have received quite limited attention. In part, this is a reflection of the fact that application of the technique is restricted to only certain types of metal complex. Nevertheless, within this limitation, it is clearly possible to use such studies to successfully address a variety of structural and other problems concerning particular complexes. There remains much scope for similar investigations in the future. Apart from such uses, LSR studies are also of considerable intrinsic interest and have wider implications for a fuller understanding of kinetic and thermodynamic aspects of metal–complex association; complex association is of fundamental importance to a variety of synthetic, electron transfer and biochemical reaction types.

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