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Mixed-ligand Lanthanide Complexes. V*. Paramagnetic Shift Induced by Yb(fod)$_3$pz in the NMR Spectrum of Benzyl Alcohol

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Hinckley demonstrated the practical application of a lanthanide chelate for inducing shifts in the NMR spectrum of cholesterol [1]. The paramagnetic tris lanthanide(III) chelates of the anion 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione, H(fod), Ln(fod)$_3$, have experienced increasing popularity particularly in the area of spectral simplification [2]. In solution paramagnetic lanthanide complexes associate with the basic functional group of organic compounds and induce isotropic hyperfine shifts in the resonance frequencies of the magnetic substrate nuclei [3]. With the lanthanides the predominant magnetic interaction is pseudo-contact in nature and the pseudo-contact shift is given by the following equation [4],

$$\left(\frac{\Delta\nu}{\nu_o}\right) = -D[(3\cos^2\Theta - 1)/R^3)]$$

where all the notations have their usual connotation. Ahmad *et al.* have demonstrated the use of seven-coordinate adducts of Ln(fod)$_3$ as the shift reagent [5] and have reported that an eight-coordinate adduct is inefficient in producing shift due to its coordinative saturation [6]. In recent reports it has been shown that even an adduct of Ln(fod)$_3$ can induce larger shifts than Ln(dpm)$_3$, where dpm is the anion of dipivalomethane, in the spectra of organic molecules [7, 8]. In this letter, I report on the paramagnetic shift induced by Yb(fod)$_3$pz, where pz stands for pyrazole, in the NMR spectrum of benzyl alcohol.

The complex was synthesized by the literature method [5]. 110 mg (1 $\times 10^{-4}$ mol) of the complex was added to a solution of benzyl alcohol (1 $\times 10^{-4}$ mol) in 0.5 ml CCl$_4$. Spectra were recorded on a Varian A 60 D NMR machine using Me$_4$Si as the internal reference.

Results and Discussion

The paramagnetic shift induced by Yb(fod)$_3$pz in the spectrum of benzyl alcohol is given in Table I.

TABLE I. Paramagnetic Shift Induced by Yb(fod)$_3$pz in the Spectrum of Benzyl Alcohol[a]

OH	CH$_2$	H$_o$	H$_m$	H$_p$
b	b	17.7	10.7	10.0

[a] Shifts in ppm (δ) downfield relative to internal Me$_4$Si. The spectrum recorded in CCl$_4$. [b] The shifts of OH and CH$_2$ protons are of course extremely large and have not been recorded.

It has been noted that the t-butyl resonance of the complex is concentration dependent and shifts slightly to the high field side as concentration is increased. In presence of complexing substrate (benzyl alcohol), the t-butyl resonance is more strongly shifted. This resonance in the complex appears at 3.72 ppm (δ) [5] in CCl$_4$ but on addition of the substrate moves to 2 00 ppm (δ). The magnitude of the shift is approximately correlated to the relative shift power of the complex [7] and is in the opposite direction. These observations together with the fact that the spectrum of the substrate is uneffected (except the shift increases with increasing amounts) by addition of any amount of the complex, show that the specific coordination of the complex to substrate occurs through the agency of oxygen lone-pair electrons and can be best rationalized in terms of a change in the coordination geometry of the complex upon association [8 9]

In the normal ^{1}H NMR spectrum of benzyl alcohol (CCl$_4$ solution) the aromatic protons coalesce and resonate as a sharp singlet at 7.36 ppm (δ) Addition of 110 mg (1 $\times 10^{-4}$ mol, 0.2 M in 0.5 ml CCl$_4$) of Yb(fod)$_3$pz greatly simplifies the spectrum to a first order analysis. All the ring protons get resolved with their positions greatly shifted to down field (Table I) The shift induced by Yb(fod)$_3$pz is larger than that induced by its europium analogue [5] but at the expense of resolution owing to the long electron relaxation time of Yb(III) ion compared to europium(III). The induced shift is larger than the shift produced by Yb(fod)$_3$pyz [7] and decreases rapidly with increasing distance. The shifts of the OH and CH$_2$ protons are of course extremely large and have not been recorded.

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