

## Mixed-ligand Lanthanide Complexes. IV\*. Paramagnetic Shift Induced by Eu(fod)<sub>3</sub>pz and Yb(fod)<sub>3</sub>pz in the NMR Spectrum of Di-1-butyl Ether

K. IFTIKHAR

Department of Chemistry, South Gujarat University, Surat-395 007, India

(Received February 24, 1986)

### Abstract

Two pyrazole adducts of Ln(fod)<sub>3</sub>, Eu(fod)<sub>3</sub>pz and Yb(fod)<sub>3</sub>pz have been scanned as potential NMR shift reagents using di-1-butyl ether. Di-1-butyl ether is a very weak donor; even then the complexes associate with the base and induce large isotropic hyperfine shifts in the resonance frequencies of the magnetic substrate nuclei. The t-butyl resonances of the complexes are strongly shifted (in the opposite direction) in the presence of the substrate. This observation together with the fact that the spectra of the substrate are unaffected by addition of any amount of the complexes are taken as evidence that the specific coordination of the complexes to the substrate occurs through the agency of oxygen lone-pair electrons.

### Introduction

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, Hfod, Ln(fod)<sub>3</sub>, have experienced increasing popularity in the area of spectral simplification [2]. In solution, paramagnetic lanthanide complexes associate with the basic functional groups of organic compounds and cause isotropic hyperfine shifts in the resonance frequencies of the magnetic substrate nuclei [3]. Metal complexes useful in this context have been called shift reagents. With the lanthanides the predominant magnetic interaction is pseudo-contact and is given by the following equation [4] where all the notations have their usual connotations.

$$\left(\frac{\Delta\nu}{\nu_0}\right) = -K_p[(3\cos^2\theta - 1)/R^3]$$

\*Part III is ref. 7.

Ahmad *et al.* have demonstrated use of seven-coordinate adducts of Ln(fod)<sub>3</sub> as shift reagents [5] and have shown that an eight-coordinate adduct is inefficient in producing shifts due to coordinative saturation [6]. In a recent report it has been shown that even an adduct of Ln(fod)<sub>3</sub> can induce larger shifts than does Ln(dpm)<sub>3</sub>, where dpm is the anion of dipivalomethane, in the spectra of organic moiety [7]. In this paper, I wish to report the shifts induced by Eu(fod)<sub>3</sub>pz and Yb(fod)<sub>3</sub>pz, where pz stands for pyrazole, in the NMR spectrum of a very weak donor, di-1-butyl ether.

### Experimental

The complexes were synthesized by the method reported in the literature [5]. 110–112 mg ( $1.0 \times 10^{-4}$  mol) of the complexes were mixed with 13 mg ( $1.0 \times 10^{-4}$  mol) of di-1-butyl ether in 0.5 ml CCl<sub>4</sub>. The spectra were recorded on a Varian A60-D NMR machine using TMS as the internal reference.

### Results and Discussion

The adducts of pyrazole, Eu(fod)<sub>3</sub>pz (**1**) and Yb(fod)<sub>3</sub>pz (**2**), have been tested with di-1-butyl ether (**A**). These pyrazole adducts are highly soluble in all organic solvents. It is worth mentioning that in presence of complexing substrate (**A**) the t-butyl resonances of the complexes are strongly shifted from the positions in the pure complexes (*i.e.*, in absence of any complexing agent) and the shift is in the opposite direction. The magnitude of the shift is approximately correlated with the relative shift power of the complexes. For example, the t-butyl resonance of **1** appears at 1.73 ppm ( $\delta$ ) in CDCl<sub>3</sub>, but on addition of **A** moves to 1.33 ppm ( $\delta$ ). This shift is concentration-dependent and increases slightly with increasing concentration of the complexes. These observations, together with the fact that spectra of substrate is unaffected (except the shift in-

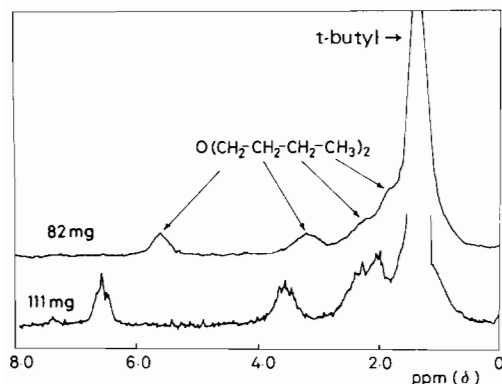


Fig. 1. 60 MHz  $^1\text{H}$  NMR spectra of di-1-butyl ether (13 mg;  $1.0 \times 10^{-4}$  mol) in 0.5 ml  $\text{CDCl}_3$  and  $\text{Eu}(\text{fod})_3\text{pz}$  (82 mg,  $7.4 \times 10^{-5}$  mol; 111 mg;  $1.0 \times 10^{-4}$  mol). Chemical shifts in ppm ( $\delta$ ) relative to internal  $\text{Me}_4\text{Si}$ .

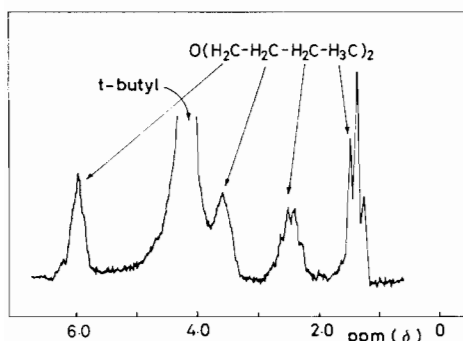


Fig. 2. 60 MHz  $^1\text{H}$  NMR spectrum of di-1-butyl ether (0.2 M) and  $\text{Yb}(\text{fod})_3\text{pz}$  (0.2 M) in  $\text{CDCl}_3$ . Chemical shifts in ppm ( $\delta$ ) relative to internal  $\text{Me}_4\text{Si}$ .

TABLE I. Paramagnetic Shifts in the Spectrum of Di-1-butyl Ether<sup>a</sup>

Complexes	$H_\alpha$	$H_\beta$	$H_\gamma$	$H_\delta$
$\text{Eu}(\text{fod})_3\text{pz}^b$	3.37	2.08	0.90	1.13
$\text{Eu}(\text{fod})_3\text{pyz}^c$	2.35	1.47	0.55	0.26
$\text{Yb}(\text{fod})_3\text{pz}^b$	2.70	2.13	0.98	0.43
$\text{Yb}(\text{fod})_3\text{pyz}^c$	8.27	6.08	2.98	1.20

<sup>a</sup>Shifts in ppm ( $\delta$ ) down-field relative to internal  $\text{Me}_4\text{Si}$ .  
<sup>b</sup>This work. <sup>c</sup>Ref. 7.

creases with increasing amounts) by addition of any amount of the complexes, show that the specific coordination of the complexes to the 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 complexes upon association [8]

The effect on the resonance positions of the different protons in A upon addition of 1 or 2 is shown in Figs. 1 and 2. The induced chemical shifts are

given in Table I. In the absence of the shift reagent the two methylene protons of A coalesce and appear at 1.45 ppm ( $\delta$ ). Upon addition of 1 or 2 the spectrum becomes amenable to a first order analysis. However, with 1 the  $\text{CH}_3$  and one of the methylene resonances are not very clear since these are partially masked by the resonance of the complex (Fig. 1). Moreover, the down-field shift induced by 2 is more convenient because the signals of the complex do not interfere (Fig. 2). Owing to the long electron relaxation time of the  $\text{Yb}(\text{III})$  ion as compared to  $\text{Eu}(\text{III})$ , it is surprising that the fine coupling is more clear when 2 is used.

It is interesting to note that the shift induced by 1 or  $\text{Eu}(\text{fod})_3\text{pyz}$  [7] (110–112 mg) in the spectrum of A is nearly equal to the shift produced by  $\text{Eu}(\text{dpm})_3$  [2] ( $1 \times 10^{-4}$  mol of A in 0.5 ml  $\text{CDCl}_3$  and saturated in  $\text{Eu}(\text{dpm})_3$ ). This large shift produced by 1 or its pyrazine analogue is due to the substitution of the fluorine moieties in Hfod, which increases both the solubility of the complexes and the residual acidity of the cation, making it a better complexing site for weak donors. Thus, it can be concluded that even an adduct of  $\text{Eu}(\text{fod})_3$  can produce larger shifts than does  $\text{Eu}(\text{dpm})_3$  which strengthens the conclusion of Rondeau and Sievers [2] that  $\text{Ln}(\text{fod})_3$  chelates are the best shift reagents of those shift reagents studied so far.

It should be mentioned that the shifts produced by pyrazine adducts [7] are much larger than the corresponding pyrazole adducts, except in case of europium complexes, where  $\text{Eu}(\text{fod})_3\text{pz}$  induced larger shifts than does  $\text{Eu}(\text{fod})_3\text{pyz}$  in the spectrum of A, benzyl alcohol or butanol [5, 7]. It is not possible to explain the reason for this behaviour in the light of these qualitative studies. However, a quantitative study, *i.e.*, the calculation of theoretical shifts and geometry, could definitely reveal the reason behind this.

## References

- 1 C. C. Hinckley, *J. Am. Chem. Soc.*, **91**, 5160 (1969).
- 2 R. E. Rondeau and R. E. Sievers, *J. Am. Chem. Soc.*, **93**, 1522 (1971).
- 3 R. von Ammon and R. D. Fisher, *Angew. Chem., Int. Ed. Engl.*, **11**, 675 (1972).
- 4 H. McConnel and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).
- 5 K. Iftikhar, M. Sayeed and N. Ahmad, *Bull. Chem. Soc. Jpn.*, **55**, 2258 (1982).
- 6 K. Iftikhar, M. Sayeed and N. Ahmad, *Inorg. Chem.*, **21**, 80 (1982).
- 7 K. Iftikhar, A. U. Malik and N. Ahmad, *J. Chem. Soc., Dalton Trans.*, 2547 (1985).
- 8 C. Brecher, H. Samelson and L. Limpicki, *J. Chem. Phys.*, **42**, 1081 (1965); G. H. Frost, F. A. Hart, C. Health and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1421 (1969).