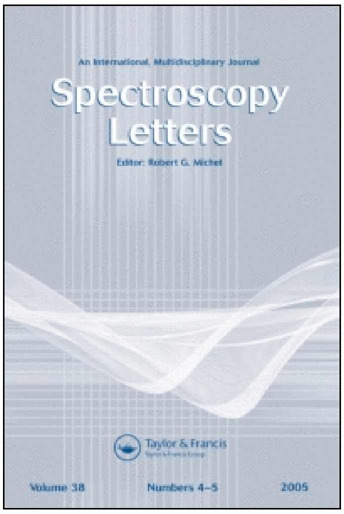

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Lanthanide Shift Reagents: Acetylacetone Complex of Yb(III) Ion

R. D. Green[a]; Shyama P. Sinha[a]
[a] Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia

To cite this Article Green, R. D. and Sinha, Shyama P.(1971) 'Lanthanide Shift Reagents: Acetylacetone Complex of Yb(III) Ion', Spectroscopy Letters, 4: 12, 411 — 417
To link to this Article: DOI: 10.1080/00387017108064675
URL: http://dx.doi.org/10.1080/00387017108064675

SPECTROSCOPY LETTERS 4(12), 411-417 (1971)

LANTHANIDE SHIFT REAGENTS: ACETYLACETONE COMPLEX OF Yb(III) ION

KEY WORDS: NMR Shift Reagents, Yb(III) acetylacetonate.

R.D. Green and Shyama P. Sinha

Department of Chemistry, University of Malaya
Kuala Lumpur, Malaysia

It has recently been shown that the 2,2,6,6-tetramethylheptane-3,5-dione (tmhd) complexes of a number of lanthanide ions possess the useful property of inducing large chemical shifts in the proton NMR spectra of certain compounds containing OH or other nucleophilic groups[1-8]. The resulting spectra are frequently more readily assignable and analysable. Although europium and praseodymium appear to be the most suitable ions for such studies, the shifting effect is also observed with other lanthanide ions.[5,6]

There has been some disagreement as to the possibility that other complexes of lanthanide ions might exhibit similar properties. Hinckley has suggested[1] that shift reagents should be relatively common among rare earth compounds, although he gives no evidence to support this postulate. On the other hand, Briggs _et al._[5] speculate that the tmhd complexes exhibit a combination of characteristics which makes their usefulness as shift reagents very unusual and rare. In support of this hypothesis, they list several rare earth compounds which do not act as shift reagents.

Considering the similar nature of the paramagnetic lanthanide complexes, we expect that shift reagents will be found among other complexes of the lanthanide ions. Indeed, Birnbaum and Moeller[9] have observed that the nitrate and perchlorate salts of Pr(III) and Nd(III) behave as shift reagents for substituted pyridines. More recent evidence[10] indicates that a variety of β-diketone complexes exhibit most or all of the desirable properties listed by Briggs *et al.*[5]

We report here preliminary studies of a lanthanide complex involving acetylacetone as ligand. The acetylacetone complex of Yb(III) was prepared by a published method[11]. Co-ordinated acetylacetone in this complex exhibits a broad resonance at δ 2.8 superimposed by a sharper peak at δ 2.55.

The normal proton NMR spectrum of benzyl alcohol in CCl_4 or $CDCl_3$ consists of three single peaks due to the OH (δ *ca.* 1.39), CH_2 (δ 4.57), and aromatic protons (δ 7.23). The addition of $Eu(tmhd)_3$ to a CCl_4 solution of benzyl alcohol was found[2] to shift the CH_2 peak far downfield; the aromatic peak was also shifted downfield and split into its *ortho*, *meta* and *para* components.

On addition of $Yb(acac)_3.H_2O$ to a $CDCl_3$ solution of benzyl alcohol, the alcohol proton signals shift downfield. At a low alcohol concentration, the OH peak is too broad to be observed; the CH_2 peak is also broadened, but is easily observable. The *ortho* proton signal is split into a doublet (J *ca.* 7 Hz) while the *meta* and *para* protons give rise to a complex resonance pattern at 60 MHz by virtue of second-order perturbations. For a 1:1 mixture of complex and alcohol, the shifts are given in Table 1, together with the

TABLE 1

Lanthanide Ion Induced Shifts in Benzyl Alcohol

Benzyl Alcohol Proton	Chemical Shift, ppm below TMS		Ratio of Induced Shifts[a]		$\underline{r}^{-3}$	
	without added complex	with added $Yb(acac)_3$	with added $Yb(acac)_3$	with[2] added $Eu(tmhd)_3$	at 2.5 Å	at 5.0 Å
CH_2	4.57	11.24	1	1	1	1
ortho	7.23	10.04	0.42	0.47	0.22	0.38
meta	7.23	8.2	0.15	0.15	0.08	0.18
para	7.23	8.0_5	0.12	0.12	0.06	0.14

a: Ratios of induced shifts and values of $\underline{r}^{-3}$ are normalised to unity for the methylene protons.

values for the free benzyl alcohol. Of course the signals due to the acac ligands do not interfere with those of the benzyl alcohol. The ratios of the shifts induced by $Eu(tmhd)_3$, as calculated from the results of Sanders and Williams[2], are also included in Table 1 for the purpose of comparing our data with those obtained for $Eu(tmhd)_3$.

In view of the geometry dependence of lanthanide ion induced shifts, the close correlation between these sets of values is suggestive that the mechanism of the paramagnetic shift is the same in each case. Of course, the absolute magnitude of the shifts is expected to be different, since the nature of the ground state is different for each ion: i.e. $^7\underline{F}_2$ for Eu(III), and $^2\underline{F}_{7/2}$ for Yb(III).

In view of an earlier assertion[3] that the Eu(III) induced shifts do not show a linear dependence on $\underline{r}^{-3}$, where $\underline{r}$ is the average distance from the ion to a particular proton, we have compared (Table 1) the ratios of the lanthanide induced shifts with the ratios of the values of $\underline{r}^{-3}$ by constructing a Dreiding model. At the van der Waals contact distance (Yb--O *ca.* 2.5 Å) the ratios of induced shift compare very poorly with the ratios of $\underline{r}^{-3}$. It is necessary to increase $\underline{r}$ to about 5 Å in order to achieve a fair correlation. Since such a long distance is not really credible in a complex of considerable stability, we conclude that the Yb(III) induced shifts are not entirely due to a pseudocontact mechanism.

Several workers[3,6] have observed a linear dependence of induced shift on the ratio of concentrations [M(III)]/[substrate] in a fairly low concentration range. We have studied the concentration dependence of the induced shift by varying the amount of benzyl alcohol added to a $CDCl_3$ solution of $Yb(acac)_3$. At higher values of [M(III)]/[substrate] we find pronounced departure from linearity (Figure 1). A similar non-linear dependence has recently been found for Eu(III) induced shifts[10].

Several possible explanations suggest themselves. The equilibrium constant for the formation of a 1:1 complex between substrate and ion may not be so high as has been previously implied[3] for similar systems. Alternatively, higher complex formation may occur at high substrate concentration, introducing the likelihood of competitive equilibrium reactions. This could involve either (a) expansion of the co-ordination shell about Yb(III) to accommodate additional alcohol molecules, or (b) displacement of one or more ligands from the ion's co-ordination shell. It is well known[12] that the lanthanide ions are capable of forming complexes with high co-ordination number and a co-ordination number of eight to

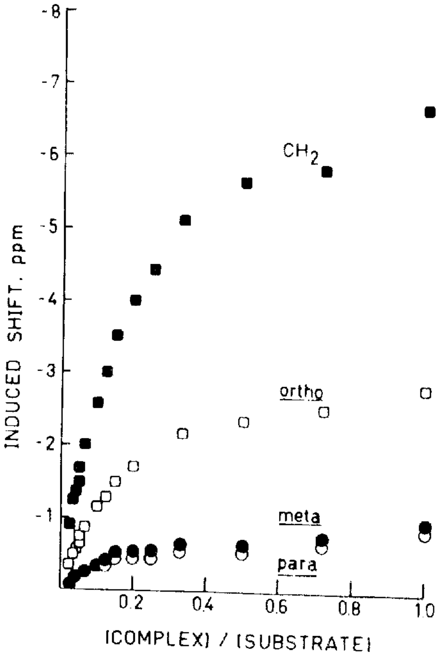

FIG. 1

Dependence of the Yb(III) Induced Shifts in Benzyl Alcohol on the ratio of [$Yb(acac)_3.H_2O$]/[alcohol].

ten is quite common among the lanthanide complexes[13]. In view of this fact, and also that we have not observed any resonance due to "free" acetylacetone, it is most unlikely that the acetylacetone ligands are displaced in significant quantities. The form of the curves in Figure 1, nonetheless, does suggest the need for caution when interpreting lanthanide induced shifts in terms of complete formation of a 1:1 complex.

Since acetylacetone would be a desirable shift reagent ligand in view of its ready availability and low price, we have surveyed the shifts induced by several of its lanthanide complexes in benzyl alcohol. The results, given in Table 2, are somewhat disappointing. The Pr complex, in particular, would be expected to induce substantial shifts, analogous to other Pr complexes[6]. The fact that it does not lead to the

TABLE 2

Shifts Induced in Benzyl Alcohol by $M(acac)_3.xH_2O$

M	Induced Shift[a], ppm			
	CH_2	ortho	meta	para
La[b]	-0.1_3	-0.1	-0.1	-0.1
Pr	0.64	0.1_7	0.0_4	0.0_4
Nd	0.15	0.0_2	0.0_2	0.0_2
Sm	-0.0_6	-0.0_8	-0.0_8	-0.0_8
Gd	broad	broad	broad	broad
Tb	broad	1.2	1.2	1.2
Ho	1.3	1.0	1.0	1.0
Yb	-6.67	-2.81	-0.97	-0.8_2

a: $[M(acac)_3.xH_2O] = [C_6H_5CH_2OH] = 0.1$ mol dm^{-3};
Solvent: $CDCl_3$

b: not paramagnetic

conclusion that acetylacetone is not as suitable as other β-diketones for a shift reagent ligand. It appears that the properties, as shifting reagents, of the lanthanide ions are strongly dependent on the nature of the ligands in their co-ordination shells.

REFERENCES

1. C.C. Hinckley, J. Amer. Chem. Soc., 91, 5160 (1969); J. Org. Chem., 35, 2834 (1970).
2. J.K.M. Sanders and D.H. Williams, Chem. Comm., 422 (1970).
3. P.V. Demarco, T.K. Elzey, R.B. Lewis and E. Wenkert, J. Amer. Chem. Soc., 92, 5734, 5737 (1970).
4. J. Briggs, F.A. Hart and G.P. Moss, Chem. Comm., 1506 (1970).
5. J. Briggs, G.H. Frost, F.A. Hart, G.P. Moss and M.L. Staniforth, Chem. Comm., 749 (1970).
6. D.R. Crump, J.K.M. Sanders and D.H. Williams, Tetrahedron Lett., 4419, 4949 (1970).
7. K.K. Andersen and J.J. Uebel, Tetrahedron Lett., 5253 (1970).
8. L.H. Keith, Tetrahedron Lett., 3 (1971).
9. E.R. Birnbaum and T. Moeller, J. Amer. Chem. Soc., 91, 7274 (1969).
10. R.E. Rondeau and R.E. Sievers, J. Amer. Chem. Soc., 93, 1522 (1971).
11. J.G. Stites, C.N. McCarty and L.L. Quill, J. Amer. Chem. Soc., 70, 3142 (1948).
12. E.L. Muetterties and C.M. Wright, Quart. Rev. (London), 21, 109 (1967).
13. S.P. Sinha, Proc. 2nd National Conf. Pure and Appl. Phys. Chem., Acad. Socialist Republic of Rumania, Bucharest, 1970; D.S. Moss and S.P. Sinha, Z. Phys. Chem. Neue Folge, 67, 330 (1969).