

LANTHANIDE-INDUCED DIFFERENTIAL SHIFTS IN N.M.R. SPECTRA OF AQUEOUS SOLUTIONS

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In solution in non-coordinating organic solvents, tris(tetramethylheptanedionato) lanthanide complexes,  $L(\text{tmhd})_3$ ,<sup>1</sup> produce large differential shifts in the  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra of alcohols, amines, ketones and other compounds,<sup>2</sup> these shifts obeying the  $(3\cos^2\chi-1)r^{-3}$  relation. No details have been reported of a comparable distance-dependent effect in aqueous solution, although shifts have been observed in the acetate  $^1\text{H}$  resonance<sup>3</sup> and in the lysozyme- $\beta$ -methyl-N-acetylglucosamine system<sup>4</sup> upon addition of lanthanide salts. Conditions in aqueous solution are rather less favourable in that hydration of the lanthanide ion prevents or greatly reduces coordination by hydroxy-, keto-, amino-, and other functions. Moreover,  $L(\text{tmhd})_3$  and many of the organic compounds whose spectra have so far been studied are insoluble in water.

Shifts in aqueous solution would be useful in allowing studies of substrates too polar to have solubility properties compatible with  $L(\text{tmhd})_3$ . More importantly, they would be useful for investigation of polyfunctional compounds containing a carboxyl group, because the shifts of these in non-polar solvents (even if soluble) would be complicated by a dynamic equilibrium between coordination by the different donor groups. In water, however, a carboxylate ion is a much better donor for lanthanides ( $\log \beta_2$  for  $\text{Pr}^{3+}/\text{CH}_3\text{COO}^- = 3.6^5$ ) than is a monodentate amine;<sup>6</sup> no stability constants for alcohols or ketones have apparently been determined, presumably because they are too low to be measured. Thus a polyfunctional carboxylic acid salt would in water be expected to coordinate to a lanthanide only by its carboxylate ion (provided that no amino or other function was favourably placed relatively to the  $-\text{COO}^-$  to exert a chelate effect). The compound should thus give simply-interpretable shifts.

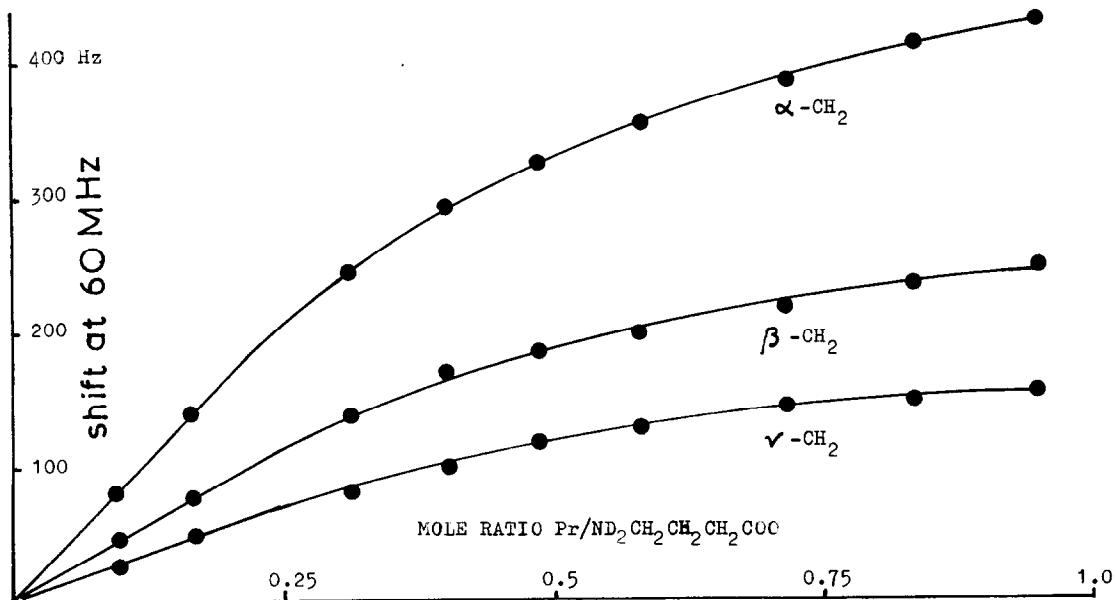
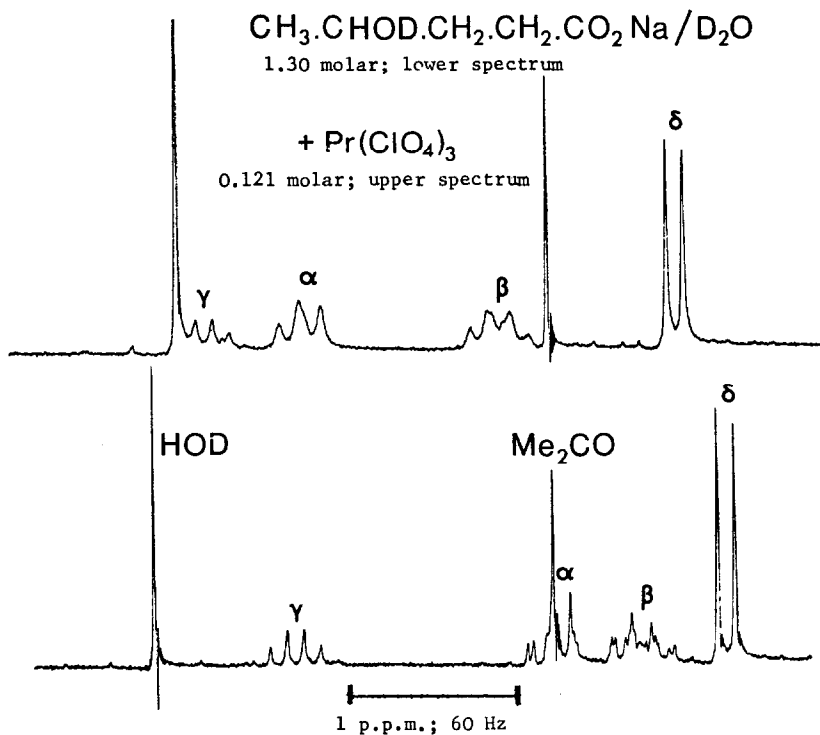
We now report unidirectional shifts in spectra of aqueous solutions of unsubstituted, hydroxy-, or amino-acid salts which convert second-order spectral features into first-order, and whose magnitude can be related to the factor  $(3\cos^2\chi-1)/r^3$ , where  $\chi$  is the off-axis angle

of the proton and  $r$  is the metal-proton distance.

Deuterium oxide solutions of propanoic acid, 4-aminobutanoic acid and 4-hydroxypentanoic acid, as salts at 0.75M - 1M concentration, were treated with increasing concentrations (up to 0.25 molar proportions) of hydrated europium or praseodymium perchlorates. Shifts of up to 4 p.p.m. were produced whose magnitudes decrease along the alkyl chain in the sequence  $\alpha > \beta > \gamma > \delta$ . Europium gives high field shifts while praseodymium gives low field shifts; these directions are opposite to those reported for  $\text{Eu}(\text{tmhd})_3$  and  $\text{Pr}(\text{tmhd})_3$  in non-aqueous solution. This reversal may be caused by changes in the  $g$ -tensor as between the two types of complex. Shifts are very nearly proportional to the mole ratio  $\text{M}^{3+}/\text{carboxylate}$  up to a mole ratio of 0.5, but strict linearity is not achieved, presumably because at the concentrations employed the lanthanide-carboxylate complex dissociates slightly. For purposes of comparison of the geometric factor  $(3\cos^2\chi-1)/r^3$  with the observed shifts we have assumed coordination by the carboxylate ligands along an axis of free-rotational pseudo-symmetry with a fully extended staggered conformation of the alkyl chain, and with bidentate coordination by the carboxylate group only. The  $\gamma\text{-NH}_2$  or  $\gamma\text{-OH}$  groups are not expected to coordinate very strongly to lanthanides in water and in this connection pH measurements indicate that the  $\gamma$ -amino group is protonated and therefore uncoordinated under our conditions, while coordination by the  $\gamma$ -hydroxy group would be expected to lead to larger shifts of the  $\delta\text{CH}_3$  resonance than are in fact observed. However, any calculation based on one particular configuration is, in the case of this very labile system, likely to be an approximation and we consider the observed agreement between the set of  $(3\cos^2\chi-1)r^{-3}$  values and the sets of shift values to be quite satisfactory. Coordination along a symmetry axis is not proved, however, by these results. Acetone was used as internal reference and relative to this the  $\text{H}_{\text{D}_2\text{O}}$  signal showed small shifts. These were of opposite sign to the shifts of the carboxylate protons, presumably because the water molecules are on average predominantly located at a considerable angular distance from the metal-carboxylate axis.

We also find that the complexes  $\text{M}\{\text{N}(\text{CH}_2\text{COO})_3\}(\text{H}_2\text{O})_3$  ( $\text{M} = \text{Y}, \text{Eu}, \text{Pr}$ ), which are insoluble in water, dissolve in solutions of sodium salts of carboxylic acids  $\text{RCOOH}$  probably owing to formation of a complex anion  $[\text{M}\{\text{N}(\text{CH}_2\text{COO})_3\}(\text{RCOO})_q\text{aq.}]^-$ . The alkyl group  $\text{R}$  then shows differential shifts for  $\text{M} = \text{Eu}, \text{Pr}$  which are of the same sign but are somewhat smaller than those induced by the corresponding lanthanide perchlorate.

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TABLE

Lanthanide-induced Shifts of Carboxylic Acids in Aqueous Solution

Acid	Additive	Shifts <sup>a</sup>			
		$\alpha$	$\beta$	$\gamma$	$\delta$
CH <sub>3</sub> CH <sub>2</sub> COOH <sup>b</sup>	Pr(ClO <sub>4</sub> ) <sub>3</sub>	134	71	-	-
	Pr{N(CH <sub>2</sub> COO) <sub>3</sub> }	66	39	-	-
NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH <sup>c</sup>	Pr(ClO <sub>4</sub> ) <sub>3</sub>	120	67	43	-
	Eu(ClO <sub>4</sub> ) <sub>3</sub>	45	28	17	-
CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> COOH <sup>b</sup>	Pr(ClO <sub>4</sub> ) <sub>3</sub>	125	69	42	21
	$(3\cos^2\chi-1)/r^3$	0.0142	0.0091	0.0051	0.0028

<sup>a</sup> Hz at 60 MHz for a lanthanide/acid molar ratio of 0.150.

<sup>b</sup> As Na salt.

<sup>c</sup> As zwitterion.

References

1. K.J. Eisentraut and R.E. Sievers, J. Amer. Chem. Soc., 1965, 87, 5254.
2. J. Briggs, F.A. Hart, G.P. Moss and E.W. Randall, Chem. Comm., 1971, 364 and references therein.
3. J. Reuben and D. Fiat, Chem. Comm., 1967, 729.
4. K.G. Morallee, E. Nieboer, F.J.C. Rossotti, R.J.P. Williams and A.V. Xavier, Chem. Comm., 1970, 1132.
5. T. Moeller, D.F. Martin, I.C. Thompson, R. Ferrús, G.R. Feistel and W.J. Randall, Chem. Rev., 1965, 65, 1.
6. D.A. Durham and F.A. Hart, J. Inorg. Nucl. Chem., 1969, 151.