Proton Chemical Shifts in Aqueous Solutions of the Rare-earth Ions as an Indicator of Complex Formations

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As part of a study of the aquo-complexes of the rare-earth ions by n.m.r. methods[1] we have examined the proton chemical shifts of aqueous solutions of a series of these ions (see Table).† The water line was usually broadened. The greatest broadening was observed for Gd^{3+} solutions, and this caused a large uncertainty in the measured shift.

Comparing the trend of the proton shifts to that of the oxygen-17 nucleus[2] in water and having in mind the large anisotropies of the g-values observed in the e.s.r. of these ions,[3] it seems that the proton shifts are dominated by contributions of pseudo-contact origin for solutions of all the paramagnetic rare-earth ions, except Gd^{III}, which is an S-state ion with isotropic g-values. In the latter case the shift is attributed to contact interaction and assuming a co-ordination number of nine the hyperfine coupling constant is found to be $A/h = -3{\cdot}4 \times 10^4$ ($\pm 35\%$) c./sec. This coupling constant is about an order of magnitude smaller than values known for the hydrates of transition-metal ions and is opposite in sign.[4]

The pseudo-contact contribution is given by[5]

$$\frac{\Delta\nu}{\nu} = -\frac{P\beta^2 J(J+1)}{45\, r^3 kT}(3\cos^2 q - 1) \times (3g_{\parallel}^2 + g_{\parallel}g_{\perp} - 4g_{\perp}^2),$$

where it is assumed that $\tau > T_{1e}$, being the correlation time for tumbling of the complex, T_{1e} the relaxation time of the unpaired electrons, P the fraction of nuclei in the first co-ordination sphere, r the distance from the metal ion to the nucleus, and θ the angle between the line joining these points and the principal magnetic axis of the complex. It has been shown by X-ray crystallography of the hydrated solid ethyl sulphates, that six of the nine water molecules form a trigonal prism around the rare-earth ion, the remaining three being in a plane with the central ion and pointing out of the faces of the prism.[6] Thus it may be anticipated that the factor $(3\cos^2\theta - 1)$ will be different for the two different (with respect to the symmetry axis) kinds of water molecules. This factor changes sign at $\theta = 54°44'$, and is negative for greater angles. The measured shift is, therefore, the algebraic sum of two contributions.

The water proton shift gradually changes upon addition of ammonium acetate (AmAc) and levels off at a value of about 3 for the ratio [AmAc]/[Ln]. The chemical shift of the acetate methyl protons varies linearly with the ratio [Ln]/[AmAc] up to a value of about 0·3 for the latter. These results clearly indicate that the acetate is bound in the first co-ordination sphere of the rare-earth ions definitely forming an "inner sphere" complex.[7] There may be some stereospecificity in removing the water from the first hydration sphere, which is expressed in the signs of the observed shifts. However, complex formation may be capable of altering the geometry of the hydration shell as well as the anisotropy of the g-values, an alteration which is difficult to determine by the methods employed in the present work.

TABLE. *Proton chemical shifts[a] in aqueous solutions of rare-earth ions*

Ln^{3+}	Aquo-complex	Acetate complex	
	H_2O[b]	H_2O[b,c]	$MeCO_2^-$[d]
La	$-$ 6·0 ± 0·5		
Pr	+ 15 ± 3	+83	−64
Nd	+ 18 ± 3	+37	−24
Sm	$-$ 5 ± 0·5		
Eu	$-$ 18 ± 3		
Gd	+ 170 ± 60		
Tb	$-$ 594 ± 15	+37	−300
Dy	$-$ 392 ± 10	+257	−497
Ho	$-$ 275 ± 6	+35	−182
Er	+ 216 ± 6	+107	+48
Tm	+ 524 ± 10		
Yb	+ 142 ± 6	+43	+64

[a] Shifts are given in c./sec. at 56·4 c./sec. relative to the resonance of the uncomplexed ligand.

[b] Interpolated values for 1 molal solutions.

[c] Shifts caused by the added $MeCO_2NH_4$ in absence of rare-earth ions where taken into account.

[d] Interpolated values for the ratio of concentrations [Ln]/[AmAc] = 0·1.

Assuming a co-ordination number of 3 with respect to acetate, a lower limit of 10^4 sec.$^{-1}$ was calculated for the rate constant of acetate exchange between the acetate complex of dysprosium(III) and the ligand in bulk. The upper limit is set by the rate constant of water exchange ($6{\cdot}3 \times 10^7$ sec.$^{-1}$),[8] obtained from ^{17}O relaxation studies.

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† The measurements were performed at ambient temperature (*ca.* 25°) at a frequency of 56·4 Mc./sec. using a Varian DP-60 spectrometer. Solutions were *ca.* 1 mole % in t-butyl alcohol, the methyl signal of which served as an internal standard.

A situation similar to that found in the acetate complexes is probably present also in other compounds. The trend of ligand and water chemical shifts observed in $(CD_3)_2SO$ solutions of rare-earth tristropolonates parallels that reported now for aqueous solutions of acetate complexes.[9]

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