Tetrahedron Letters No.50, pp. 4419-4422, 1970. Pergamon Press. Printed in Great Britain.

EVALUATION OF SOME TRIS(DIPIVALOMETHANATO) LANTHANIDE COMPLEXES AS PARAMAGNETIC SHIFT REAGENTS

D. R. Crump, J. K. M. Sanders and Dudley H. Williams
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

(Received in UK 21 September 1970; accepted for publication 1 October 1970)

There has been a great deal of interest recently in paramagnetic shift reagents which produce spectral simplifications in the pmr spectra of alcohols and other lone pair bearing organic molecules.[1,2,3] These reagents are paramagnetic tris(dipivalomethanato) lanthanide complexes with an ability to expand their coordination. We wish now to report the shift characteristics of several other complexes[4] conforming to this definition, and in the accompanying communication to describe some of the important applications made possible by the more quantitative analyses we have developed elsewhere.[5]

The table shows (a) the previously unreported resonance positions of the t-butyl groups of the pure paramagnetic complexes in CCl_4 solution (at approximately 0.05M concentration), (b) shift power relative to $Eu(DPM)_3$ (positive is downfield, negative is upfield), (c) reported[3] relative shifts in $M[OP(NMe_2)_3]_4(ClO_4)_3$, (d) broadening in Hz/(Hz of shift) as determined for the methyl resonance of a 0.10M solution of t-butanol in CCl_4. The chosen complexes constitute a representative selection of lanthanides in terms of position in the periodic table, expected shift power,[3] and expected line broadening properties.[3,6] Relative shift powers have been calculated from the gradients of the straight lines obtained by plotting shift *vs* molar ratio $[M(DPM)_3]/[substrate]$.

Table

Shift Characteristics of some Lanthanide Complexes

Metal (M) in complex	t-Butyl resonance in complex (δ)	Approx. shift power rel. Eu(DPM)$_3$	Shift in M[OP(NMe$_2$)$_3$]$_4$(ClO$_4$)$_3$ rel. to M=Eu	Broadening [Hz/(Hz of shift)]
Pr	+1.4	-1.1	-2.25	0.005
Sm	+1.0	-0.2	-0.2	0.02
Eu	+0.5	+1.0	+1.0	0.003
Tb	(17)	-5.5	-14.4	0.1
Ho	+5.9	-7	-12.8	0.02
Yb	-0.3	+4	+5.0	0.02

The gradients are fairly sensitive to change in substrate concentration and therefore the same concentration of a given substrate was used with each of the complexes. Substrates used were benzyl alcohol, 4-*t*-butylcyclohexanone, dimethyl tetradecandioate and *n*-pentylamine. While the relative shift powers of the complexes vary slightly with different substrates (the figures in the table are typical values), the shift ratios of protons in any given substrate remain the same whichever lanthanide is used. This implies that the associated adducts have essentially the same shape and stoicheiometry for all the metals and that only the strength and direction of the ion's magnetic field is varying. Whichever M(DPM)$_3$ is actually used, all the analyses and discussion of reference 5 remain valid and results for one complex are readily converted into those for another complex by the application of the relative shift powers.

The shift of the *t*-butyl resonance of the pure paramagnetic β-diketone complexes in CCl$_4$ from the diamagnetic position [La(DPM)$_3$:1.1δ[4]] is concentration dependent and increases slightly as the concentration is increased. In the presence of complexing substrates, the t-butyl resonance is more strongly shifted from the diamagnetic position. The magnitude of the shift from the diamagnetic position is approximately correlated with the relative shift power of the complex and is in the opposite direction. For example, the t-butyl resonance of $Eu(DPM)_3$ occurs at 0.5 δ in a 0.05M solution in CCl_4 (Table), but on addition of alcohols or amines (0.1-0.3M) moves to -1 to -2 δ.

The broadening observed with Eu and Pr complexes is such that the gross multiplet structure frequently remains observable even for relatively large shifts, but the fine structure is rapidly lost when the other metal complexes are used. Except for the case of Tb, broadening of non-shifted resonances is normally very small (provided that all traces of insoluble oxide have been removed by sublimation). It is noteworthy that the colours of the anhydrous, freshly sublimed complexes are pale green (Pr), white (Sm, Tb, Yb), pale yellow (Eu), and pink-yellow (Ho). After the absorption of atmospheric moisture (detrimental!), the colours of the Pr and Eu complexes are respectively yellow and white.

$Eu(DPM)_3$ is generally the most useful paramagnetic shift reagent (P.S.R.) because the t-butyl resonance of the complex appears above TMS and thus does not interfere. The downfield shifts are more convenient for locked instruments and reinforce the inductive effect of electronegative functional groups. $Pr(DPM)_3$ is a useful complement to $Eu(DPM)_3$, especially for the observation of methyl groups in steroids. However, in the presence of substrates, the t-butyl resonance of $Pr(DPM)_3$ occurs in the 3-5 δ range and can mask resonances of interest in some cases.

Acknowledgements D.R.C. thanks the Commissioners for the Exhibition of 1951 for the award of a scholarship. J.K.M.S. thanks the S.R.C. for a maintenance grant.

References

1. C. C. Hinckley, J. Amer. Chem. Soc., 91, 5160 (1969).
2. J. K. M. Sanders and D. H. Williams, Chem. Commun., 422 (1970).
3. J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss and M. C. Staniforth, Chem. Commun., 749 (1970).
4. K. S. Eisentraut and R. E. Sievers, J. Amer. Chem. Soc., 87, 5254 (1965); Inorg. Synth., XI, 94 (1968).
5. J. K. M. Sanders and D. H. Williams, J. Amer. Chem. Soc., in the press.
6. J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, 1959, p. 210.