Tetrahedron Letters No. 30, pp. 2813-2816, 1971. Pergamon Press. Printed in Great Britain.

Evidence for Contact and Pseudo-Contact Contributions in Lanthanide-Induced ^{31}P N.M.R. Shifts

Jeremy K. M. Sanders and Dudley H. Williams

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

(Received in UK 16 June 1971; accepted in UK for publication 24 June 1971)

The remarkable p.m.r. shift properties of $Eu(DPM)_3$ and related compounds have recently been extensively studied,[1-4] and have been employed successfully to solve several otherwise difficult problems.[5-8] With few exceptions, however, published work in this field has been largely descriptive, and in our recent studies we have been investigating the hitherto neglected area of the actual physical processes involved: the analysis of stoichiometry and equilibria for mono- and bi-functional systems, the solution dimerisation of $Eu(DPM)_3$, variation of angular variables leading to upfield shifts.[9] We have also found that $Eu(NO_3)_3.6D_2O$ is an effective shift reagent in aqueous and polar solution for the functional group $X\text{-}O^-$ (where $X = R\text{-}\overset{O}{\overset{\|}{C}}\text{-}$, $R_3\overset{+}{P}\text{-}$, $R_3\overset{+}{As}$), giving sizeable upfield shifts in ^1H spectra.[10] Details of the usefulness of this compound (and the Pr analogue giving reverse shifts) will be given elsewhere,[9] but we present here results of a ^1H and ^{31}P study which demonstrate a contact contribution to the observed ^{31}P shifts in phosphates and phosphonates.[†]

[†] The distinction between contact (CS) and pseudo-contact (PCS) shifts cannot be stressed too strongly:[11] a PCS is caused by a local dipolar magnetic field which either supplements or opposes the applied magnetic field. A CS arises by delocalisation of electron density between the metal ion and the substrate molecular orbitals, i.e. from some degree of covalent bonding.

Table: Shifts induced by addition of lanthanide nitrates to substrates

	^{1}H GRADIENTS* (p.p.m.)			^{1}H Δ(lim)* (p.p.m.)			^{31}P GRADIENTS** (p.p.m.)		
	Eu	Pr	Pr/Eu	Eu	Pr	Pr/Eu	Eu	Pr	Pr/Eu
I	<0.1	-	-	-	-	-	$<\pm 10$	-	-
II	v.small	-	-	-	-	-	-505 ± 15	250 ± 5	-0.50 ± 0.02
III							-540 ± 30	270 ± 10	-0.50 ± 0.05
CH_2	-0.5 ± 0.1	+1.7	-3.4 ± 0.7	-0.35	1.1	-3.1			
IV							-470 ± 25	285 ± 10	-0.61 ± 0.05
CH_2	-2.2	6.0	-2.7	-1.17	2.8	-2.4			
CH_3	-0.7	2.1	-3.0	-0.36	1.0	-2.8			
CH_2'	-3.1	9.5	-3.1	-	3.8	-			
CH_3'	-1.4	3.9	-2.8	-	1.6	-			

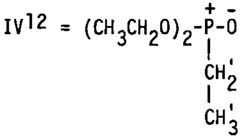
* Determined at 100 MHz, 0.4-0.5 molar solutions in d_6-acetone

**Determined at 40.5 MHz, 2.5-3.0 molar solutions in d_6-acetone

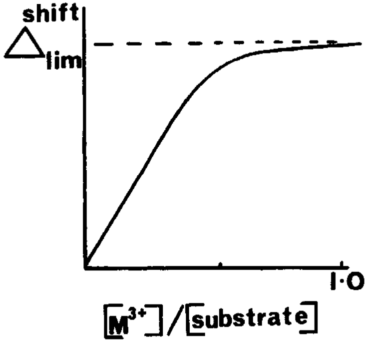
I = $(EtO)_3P$

II = $(MeO)_3\text{-}\overset{+}{P}\text{-}\overset{-}{O}$

III = $(EtO)_3\text{-}\overset{+}{P}\text{-}\overset{-}{O}$



$IV^{12} = (CH_3CH_2O)_2\text{-}\overset{+}{P}(CH_2'CH_3')\text{-}\overset{-}{O}$



The Table shows observed gradients (of the straight line section of the plot - see figure) and the observed limiting proton shifts, Δ(lim). ^{31}P shifts are relative to internal 0.5M triphenylphosphine, which is shown not to interact with the lanthanide nitrates by the following evidence: (a) no observable shifts are observed with PPh_3 {or its derivatives with assignable protons, e.g. tri(p-anisyl)phosphine} up to mole ratios of 1.0, (b) addition of traces of the broadening probe $Gd(NO_3)_3.6H_2O$ causes the PPh_3 resonance to broaden only at the same rate as TMS, whereas all complexing substrates broaden much more rapidly.

The proton shifts of both III and IV follow the shape shown in the figure for interaction with both the Eu and Pr compounds which indicates that in each case basically the same interaction is occurring *via* the P-O^- group (the phosphite, I, being inactive) and calculations[9] indicate that the data are consistent with the major process being as shown in (i), K being of the order 50-300.[13] In addition, the consistent Pr/Eu shift ratios in the

$$2R_3PO \ + \ M^{3+} \ \overset{K}{\rightleftharpoons} \ \{M(R_3PO)_2\}^{3+} \qquad \text{(i)}$$

proton spectra indicate that substantially the same complexes are being formed with each metal, and that the shifts are pseudo-contact in origin. If the ^{31}P resonances were similarly affected only by PCS then one would expect[2] to find a Pr/Eu shift ratio of *ca* -2.9 but in fact we find -0.5 to -0.6. It has been shown[2] that there is no significant CS contribution to the ^{13}C or ^{1}H proton shifts in the borneol-$M(DPM)_3$ system, but recent results[14] for the amine-$M(DPM)_3$ system are clearly best explained in terms of a dominating CS in the ^{14}N spectrum.

In order to explicitly separate the CS and PCS contributions in these cases it is necessary to know the values of $g_{av}J(J+1)$ for both metal ions, as this is equal to the ratio of the induced contact shifts.[15] The induced PCS ratio is presumably *ca* -2.9 and hence simultaneous equations should readily yield the relative contributions in both the ^{14}N and ^{31}P cases. Eu^{3+}, however, is unsuitable for e.s.r. determinations of g_{av} and we are hoping, therefore, to re-investigate the reaction with, for example, Nd^{3+} or Sm^{3+}.[15]

Acknowledgement. J.K.M.S. thanks the S.R.C. for a maintenance grant.

References

1. J. K. M. Sanders and D. H. Williams, J. Amer. Chem. Soc., 1971, 93, 641 and references therein.
2. J. Briggs, G. P. Moss, F. A. Hart and E. W. Randall, Chem. Commun., 1971, 364.
3. R. E. Rondeau and R. E. Sievers, J. Amer. Chem. Soc., 1971, 93, 1522.
4. G. M. Whitesides and D. W. Lewis, J. Amer. Chem. Soc., 1970, 92, 6979.
5. M. R. Willcott, J. F. M. Oth, J. Thio, G. Plincke and G. Schroder, Tetrahedron Letters, 1971, 1579.
6. C. P. Casey and C. R. Cyr, J. Amer. Chem. Soc., 1971, 93, 1280.
7. Z. W. Wolkowski, Tetrahedron Letters, 1971, 825.
8. L. H. Keith, Tetrahedron Letters, 1971, 3.
9. Manuscript in preparation.
10. See also (a) J. Reuben and D. Fiat, J. Chem. Phys., 1969, 51, 4909 and references therein.
    (b) K. G. Morallee, E. Nieboer, F. J. C. Rossotti, R. J. P. Williams, A. V. Xavier and R. A. Dwek, Chem. Commun., 1970, 1132.
11. E. de Boer and H. van Willigen, Prog. Nucl. Mag. Resonance Spectroscopy, 1967, 2, 111.
12. F. G. Mann and B. C. Saunders, "Practical Organic Chemistry", 4th Edn., Longmans, 1960, p. 309.
13. This analysis yields only an apparent K which neglects the D_2O, acetone or NO_3^- displaced from the metal ion coordination sphere.
14. M. Witanowski, L. Stefaniak, H. Januszewski and Z. W. Wolkowski, Tetrahedron Letters, 1971, 1653.
15. E. R. Birnbaum and T. Moeller, J. Amer. Chem. Soc., 1969, 91, 7274.