A Nuclear Magnetic Resonance Investigation of Bis(*OO'*-diethyl dithiophosphato)-complexes of the Lanthanoids: Separation of Contact and Pseudo-contact Contributions to the Chemical Shifts

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Measurements of ^1H and ^{31}P chemical shifts have been made at 26 and −40 °C for $[AsPh_4][Ln\{S_2P(OEt)_2\}_4]$ (Ln = La–Lu, excluding Pm and Gd). The results show that there are two structure types in solution, La–Dy and Ho–Lu. In both series the ^1H shifts are dipolar in origin, but the ^{31}P shifts have a large contact contribution. A new approach to the determination of the contact contribution has been developed, and hyperfine coupling constants of 1.52 and 0.86 MHz obtained for the two structure types. This is interpreted as a covalent contribution to the bonding.

We recently reported the preparation and characterization of a number of dithiophosphate complexes of the lanthanoids.[1] Analogous complexes have also been reported by Das *et al.*[2] Although the available structural and spectroscopic evidence may be interpreted as indicating a covalent contribution to the bonding, the interpretations are not unequivocal.

Evidence for covalent bonding is the demonstrated presence of ligand electrons on the metal ion or metal electrons on the ligand. The lanthanoids comprise a series of ions containing unpaired *f* electrons and the dithiophosphinate ligands contain two nuclei with spin $I = \frac{1}{2}$, ^1H and ^{31}P. Due to the rapid electronic relaxation of the paramagnetic lanthanoids the above system lends itself to investigation by n.m.r. spectroscopy.[3] The presence of covalent bonding may be inferred if there is a direct hyperfine interaction between the spin of the unpaired electrons of the metal and the spin of the ligand nuclei.

The chemical shift of a particular nucleus in a paramagnetic complex with respect to a diamagnetic analogue is composed of two contributions. These are a pseudo-contact shift, which is dipolar in origin,[3] and the contact shift due to hyperfine coupling. There has been much recent interest in separating these two effects. The main focus has been on lanthanoid shift reagents and the structural information available from the geometrical parameters derived from the pseudo-contact shift. One method of separating the two effects has been reported by Dobson *et al.*[4] We have developed a second approach which gives a better value for the contact shift and a direct measure of the hyperfine coupling constant. The theoretical derivation of this approach, and the results of the measurements, are presented herein.

THEORY

The isotropic shift, $\Delta\nu$, is defined as the difference in resonance frequency between a nucleus bound in a paramagnetic complex and the same nucleus in an analogous diamagnetic complex. In general, the isotropic shift of nuclei in paramagnetic lanthanoid complexes is given by the sum of the Fermi-contact and the pseudo-contact interactions. The total shift is thus given by (1) where Δ_t is

$$\Delta_t = \Delta_c + \Delta_{pc} \qquad (1)$$

$\Delta\nu/\nu_0$. Reuben and Fiat[5] calculated the appropriate form (2) of the contact shift for nuclei in lanthanoid complexes where A/h is the scalar coupling constant in Hz and

$$\Delta_c = \frac{2\pi\beta J(J+1)g_L(g_L-1)}{3kT\gamma_N}\cdot\frac{A}{h} \qquad (2)$$

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[1] (*a*) A. A. Pinkerton, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 495; (*b*) A. A. Pinkerton and D. Schwarzenbach, *J.C.S. Dalton*, 1976, 2464, 2466; (*c*) Y. Meseri, A. A. Pinkerton, and G. Chapuis, *ibid.*, 1977, 725; (*d*) A. A. Pinkerton, Y. Meseri, and C. Rieder, *ibid.*, 1978, 85.

[2] P. N. Mohan Das, W. Kuchen, H. Keck, and C. Hägele, *J. Inorg. Nuclear Chem.* 1977, **39**, 833.

[3] R. E. Sievers, ' Nuclear Magnetic Resonance Shift Reagents,' Academic Press, New York, 1973.

[4] C. M. Dobson, R. J. P. Williams, and A. V. Xavier, *J.C.S. Dalton*, 1973, 2662.

[5] J. Reuben and D. Fiat, *J. Chem. Phys.*, 1969, **51**, 4909.

g_L is the Landé g factor, all the other symbols having their usual meaning.* Bleaney [6] developed a simple theory of pseudo-contact shifts for lanthanoid complexes having axial symmetry, resulting in equation (3) for the pseudo-

$$\Delta_{pc} = \frac{g^2\beta^2 J(J+1)(2J-1)(2J+3)D_z(3\cos^2\theta - 1)}{60(\boldsymbol{k}T)^2 r^3} \quad (3)$$

contact shift, where D_z is the axial component of the zero-field splitting tensor and θ is the angle between the vector of length r joining the nucleus to the metal ion and the principal axis of symmetry.

Dobson *et al.*[4] used the above equations in the study of the shifts of ^1H and ^{31}P in lanthanoid complexes of cytidine-5′-monophosphate and separated the contact and pseudo-contact contributions to the ^{31}P shift. Their primary interest was to determine the pseudo-contact interaction and thus obtain structural information. The equations derived below are a modification of their approach because our interest is primarily in obtaining the value of the scalar coupling constant and thus inferring the relative covalency of the metal–ligand bond. The resulting equations and graphical representation are somewhat more sensitive to structural changes about the lanthanoid ions than is Dobson's representation.

In accordance with the results of ^{17}O magnetic resonance studies by Reuben and Fiat [5] and the theoretical considerations of Lewis *et al.*,[7] we assume that the scalar coupling constant does not change significantly within a series of isomorphous lanthanoid complexes containing the same ligand. Following Dobson *et al.*[4] and using equation (3), we define the ratio of the pseudo-contact shifts of two different nuclei within the same complex as in (4). Since

$$\Delta_{pc}{}^i : \Delta_{pc}{}^j = R_{ij} = \frac{3\cos^2\theta_i - 1}{r_i{}^3} : \frac{3\cos^2\theta_j - 1}{r_j{}^3} \quad (4)$$

this ratio is independent of the lanthanoid ion chosen and is only a function of the structural parameters θ and r, it should be a constant within an isomorphous series of lanthanoid complexes containing the same ligand. If we let the nucleus j be the methyl or methylene protons in the ethoxy-group of the dithiophosphate ligand studied and assume that the contact interaction between the lanthanoid and the proton is negligible, then equation (1) can be applied to the phosphorus nucleus, i, and rewritten as (5).

$$\Delta_t{}^i = \Delta_c{}^i + R_{ij}\Delta_t{}^j \quad (5)$$

Then rewriting equation (2) in a simpler form (6) with

$$\Delta_c{}^i = KJ(J+1)g_L(g_L - 1)(A/h) \quad (6)$$

$K = 2\pi\beta/3\boldsymbol{k}T\gamma_N$ and inserting equation (6) into (5) and rearranging to give (7), a plot of $\Delta_t{}^i/[KJ(J+1)g_L(g_L-1)]$

$$\frac{\Delta_t{}^i}{KJ(J+1)g_L(g_L-1)} = \frac{A}{h} + \frac{R_{ij}\Delta_t{}^j}{KJ(J+1)g_L(g_L-1)} \quad (7)$$

against $\Delta_t{}^j/[KJ(J+1)g_L(g_L-1)]$ should give a straight line of gradient R_{ij} and intercept A/h.

The assumption that the shifts of the protons in the dithiophosphate ligands are entirely due to pseudo-contact shifts can be verified by a technique suggested by Bleaney.[6] The equation for the pseudo-contact shift [equation (3)] can be rewritten as (8) to include the crystal-field parameters in place of the z component of the zero-field splitting tensor. Using this relation it can be seen that, within a series of isomorphous complexes, the ratio of the

$$\Delta_{pc} = \frac{g^2\beta^2(3\cos^2\theta - 1)}{60(\boldsymbol{k}T)^2 r^3}(2A_2{}^0)\langle r^2\rangle J(J+1)(2J-1)(2J+3)\langle J\|\alpha\|J\rangle \quad (8)$$

shifts of two different protons should remain constant on changing the lanthanoid ion. Additionally, a plot of the chemical shift of the protons at constant temperature against Bleaney's tabulated values [6] of $g^2J(J+1)(2J-1)(2J+3)\langle J\|\alpha\|J\rangle$ should give a straight line if there is no contact contribution to the shift.

EXPERIMENTAL

The crystalline complexes $[AsPh_4][Ln\{S_2P(OEt)_2\}_4]$ were prepared by the technique reported in the literature.[1] All the samples for n.m.r. investigation were prepared by addition of CD_2Cl_2 (C.E.A. France; dried over 4-Å molecular sieves) to the crystalline salt in an inert atmosphere. Samples prepared for chemical-shift measurements were *ca.* 2 mol dm^{-3} in the lanthanoid(III) salt of interest and *ca.* 1 mol dm^{-3} in $[La\{S_2P(OEt)_2\}_4]^-$ as an internal reference for both the ^{31}P and ^1H spectra. A trace of $SiMe_4$ was added to the solution as an additional reference for the proton spectra. The ^{31}P spectra of the salts of La^{3+} and Lu^{3+} were measured using a capillary of 85% H_3PO_4 as an external reference in order to establish the chemical shifts relative to a standard reference peak.

All the n.m.r. spectra were recorded on a Bruker WP-60 n.m.r. spectrometer equipped with a variable-temperature accessory and multinuclear capability. The proton spectra were recorded at 60 MHz, the ^{31}P spectra at 24.3 MHz with broadband proton decoupling to simplify the signal shape. The spectra were recorded using quadrature detection and *ca.* 1 000 scans for the ^{31}P spectra and 40 scans for the ^1H spectra. The sweep width and pulse-repetition rate were varied depending on the chemical shift and approximate relaxation times. The technique used to obtain the spectra was to record the ^{31}P spectra of several samples at 26 and −40 °C in 10-mm n.m.r. tubes. The samples were then transferred to 5-mm tubes in an inert atmosphere, the spectrometer switched to proton operation, and the ^1H spectra recorded at 26 and −40 °C. In this manner, all the spectra for a given lanthanoid were recorded on the same sample within a relatively short period of time, thus eliminating problems of hydrolysis.

RESULTS AND DISCUSSION

Most studies of lanthanoid shifts reported in the literature have involved measurements of isotropic shifts of nuclei in ligands which are rapidly exchanging with the lanthanoid complex. In these cases, the chemical shift measured is attenuated by the ratio of the bound to bulk ligand concentrations. The shifts measured in this study are in the absence of chemical exchange and thus are independent of concentration. It was deemed necessary to verify the absence of chemical exchange. This was accomplished by preparing two n.m.r. samples containing both the complex $[Ce\{S_2P(OEt)_2\}_4]^-$ and the free ligand $[S_2P(OEt)_2]^-$, where the mol ratios of free

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* The difference in sign between our equations and those in refs. 5 and 6 is due to our assignment of downfield shifts as positive.

[6] B. Bleaney, *J. Magnetic Resonance*, 1972, **8**, 91.

[7] W. B. Lewis, J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, 1962, **36**, 694.

ligand to complex were 0.530 and 1.08 : 1. The ^{31}P spectra of these two mixtures were recorded at several temperatures between 26 and −40 °C. The ^{31}P linewidths of the more concentrated sample were insignificantly but consistently larger than those of the sample containing a lower concentration of free ligand, but the chemical shifts were identical within experimental error. These results were interpreted to mean that there was negligible chemical exchange in the test solutions. The rate of exchange in the samples used for the shift measurements should be even lower due to the virtual absence of free ligand. Nevertheless, it was decided to obtain chemical shifts at two widely different temperatures in order to be doubly certain of the results and to increase the number of chemical shifts available.

TABLE 1

Chemical shifts (p.p.m.) of the diamagnetic complexes *

	At 26 °C			At −40 °C		
	δ(CH_2)	δ(CH_3)	δ(P)	δ(CH_2)	δ(CH_3)	δ(P)
$[La\{S_2P(OEt)_2\}_4]^-$	4.10	1.23	100.12	4.11	1.25	99.88
$[Lu\{S_2P(OEt)_2\}_4]^-$	4.17	1.29	100.37	4.18	1.26	99.47

* Downfield shifts are reported as positive; ^1H shifts are relative to internal $SiMe_4$ and ^{31}P shifts relative to an external capillary of 85% H_3PO_4.

It is widely believed that even in kinetically stable lanthanoid complexes the first co-ordination sphere is highly fluxional,[8] resulting in rapid averaging of the resonances of nuclei which, although in analogous positions in the free ligands, may be rendered inequivalent by complexing to the metal ion. The structure of the $[Pr(S_2PMe_2)_4]^-$ anion [1b] is known and the methyl protons should be chemically inequivalent. Assuming that the structures of the $[S_2P(OEt)_2]^-$ complexes are similar, some inequivalency of the protons would be expected. The proton spectra of the diamagnetic complexes of La^{3+} and Lu^{3+} show only one multiplet each for the methylene and methyl protons. The chemical shifts reported in Table 1 indicate that the motionally averaged chemical shift of the protons and the phosphorus are identical within experimental error for both complexes.

TABLE 2

Isotropic shifts of the paramagnetic lanthanoid complexes [a]

	At 26 °C			At −40 °C			
Metal	$10^6\ \Delta(CH_2)$	$10^6\ \Delta(CH_3)$	$10^6\ \Delta(P)$	$10^6\ \Delta(CH_2)$	$10^6\ \Delta(CH_3)$	$10^6\ \Delta(P)$	$\frac{10^8 KTJ(J+1)g_L(g_L-1)}{Hz^{-1}\ K}$
Ce	−1.41	−0.49	−98.38	−2.47	−0.85	−122.76	−1.392
Pr	−3.42	−1.25	−263.71	−6.31	−2.21	−348.44	−4.157
Nd	−1.76	−0.61	−355.88	−3.28	−1.14	−466.42	−6.377
Sm	−0.27	−0.10	9.79	−0.33	−0.12	−15.88	−2.320
Eu	1.75	0.62	562.63	3.00	1.04	653.66	*b*
Tb	−34.25	−13.26	1 463.17	−60.14	−23.32	1 832.55	40.917
Dy	−39.70	−15.09	1 150.99	−73.52	−25.88	1 446.75	36.804
Ho	−15.52	−5.86	843.91	−28.76	−10.45	1 057.78	29.227
Er	11.18	4.31	577.33	20.92	7.84	757.70	19.874
Tm	14.82	5.61	322.22	27.43	10.26	443.05	10.608
Yb	4.66	1.59	96.46	10.48	3.76	135.14	3.340

[a] Downfield shifts are reported as positive. All the shifts were measured relative to the corresponding nucleus of the diamagnetic complex $[La\{S_2P(OEt)_2\}_4]^-$ as internal reference. [b] The Eu^{3+} ion has a ground state with $J = 0$ and the paramagnetism arises from thermally populated excited states.

The original intention of this study was to separate the pseudo-contact and average contact shift for the series of lanthanoid complexes and to compare the average scalar coupling constant with other metal–ligand scalar coupling constants. It was hoped that this comparison would yield some information about the covalency of the metal–ligand bond relative to other known metal complexes. The relatively high polarizability of the sulphur atom, combined with the bidentate nature of the dithiophosphate ligand, should give a system with a fairly large covalent contribution to the metal–ligand bond. The existence of a sizeable scalar coupling constant implies a significant probability of finding the paramagnetic electrons at the position of the ligand nucleus or of ligand electrons being in empty or half-filled metal orbitals. Either of these situations implies the existence of covalency in the Ln^{3+} metal–ligand bond.

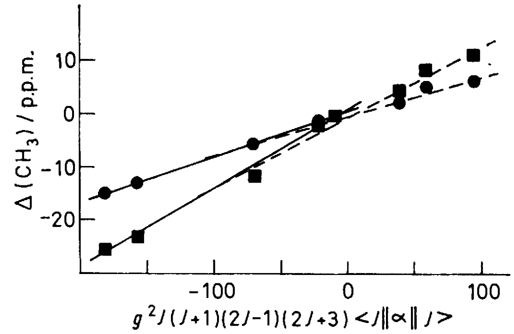

FIGURE 1 Methyl-proton chemical shift relative to $[La\{S_2P(OEt)_2\}_4]^-$ plotted against $g^2J(J + 1)(2J - 1)(2J + 3)\langle J\|\alpha\|J\rangle$ from ref. 6 at 26 (●) and −40 °C (■): (——) Ce—Dy; (– – – –) Ho—Yb

Figures 1 and 2 show plots of the proton chemical shifts of the methyl protons and of the methylene protons against the quantity $g^2J(J + 1)(2J - 1)(2J + 3)\langle J\|\alpha\|J\rangle$ obtained from Bleaney's discussion of lanthanoid shifts.[6] It can be seen that the points might well be fitted to a single straight line for each independent

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[8] R. C. Fay, D. G. Lewis, and J. R. Weir, *J. Amer. Chem. Soc.*, 1975, **97**, 7179 and refs. therein.

series of shifts, as predicted by Bleaney. This is the interpretation that we reported in a previous article on the basis of only proton data.[1d] Now, however, based on the combined ^1H and ^{31}P chemical-shift data, we have chosen to split the lanthanoid series into light (Ce–Dy) and heavy metals (Ho–Yb). The exact reason for this will be discussed below, but it is clear that by so doing somewhat better straight lines are obtained. In any case, the linear relation indicates that the proton chemical shifts are almost entirely due to a pseudo-contact interaction. This dipolar nature of proton shifts has been noted and discussed previously.[9]

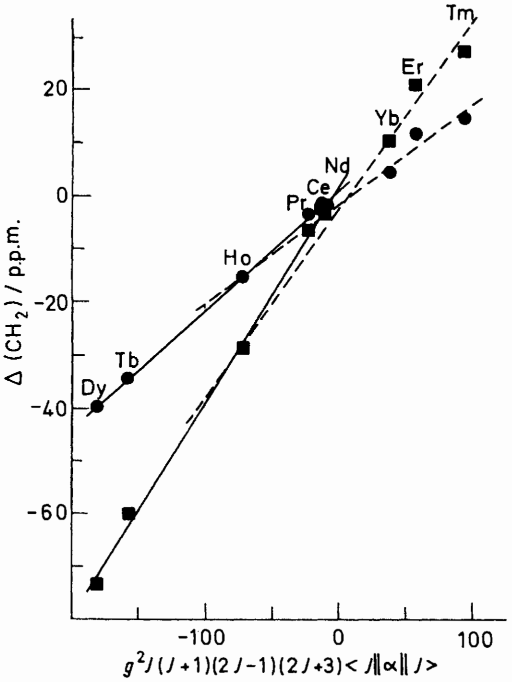

FIGURE 2 Chemical shift of CH_2 relative to $[La\{S_2P(OEt)_2\}_4]^-$ plotted against $g^2J(J+1)(2J-1)(2J+3)\langle J\|\alpha\|J\rangle$ from ref. 6. For details see Figure 1

A plot of the ^{31}P against the ^1H chemical shift divided by the appropriate series of constants should give a straight line for an isomorphous series of lanthanoid complexes as was pointed out in equation (7). Figures 3 and 4 show such plots for the methyl and methylene protons. This method of plotting the data is particularly sensitive to the assumption that the entire series of lanthanoid complexes is isomorphous. The data are interpreted to mean that there is a change in the solution structure between dysprosium and holmium. The result is that each Figure is relatively well described by two straight lines, which have been least-squares fitted to the data. The shifts for samarium and europium are not included on the plots because these two ions have a significant thermal population of excited states and therefore do not fit within the theoretical model.[6] As pointed out in the Theory section, the intercepts of the lines in Figures 3 and 4 should correspond to the scalar coupling constant, A/h, in Hz. The scalar coupling constant found for the light lanthanoids using the methyl proton shift (Figure 3) is 1.51 MHz and using the methylene proton shift (Figure 4) is 1.53 MHz, yielding an average scalar coupling constant of 1.52 MHz for the ^{31}P lanthanoid scalar interaction. Similarly, the scalar coupling constant for the heavy lanthanoids is 0.863 and 0.864 MHz derived from the methyl and methylene shifts respectively. The lower value of the scalar coupling constant in the heavy lanthanoids can be understood to mean that there is a lower fractional spin occupancy on the phosphorus atom in these complexes, or equivalently a less covalent bond between the lanthanoid metal ion and the phosphorus nucleus in the ligand. As discussed in the

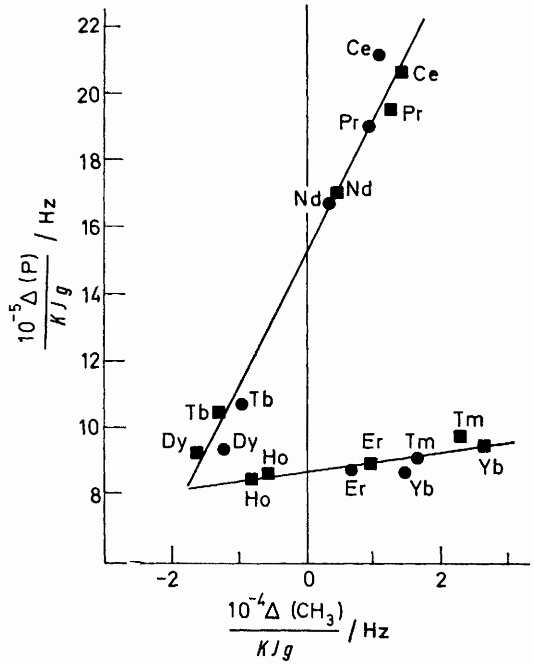

FIGURE 3 Plot of $\Delta(P)/KJg$ against $\Delta(CH_3)/KJg$ at 26 (●) and −40 °C (■) where the shifts are relative to $[La\{S_2P(OEt)_2\}_4]^-$ and $KJg = 2\pi\beta J(J+1)g_L(g_L-1)/3kT\gamma_N$

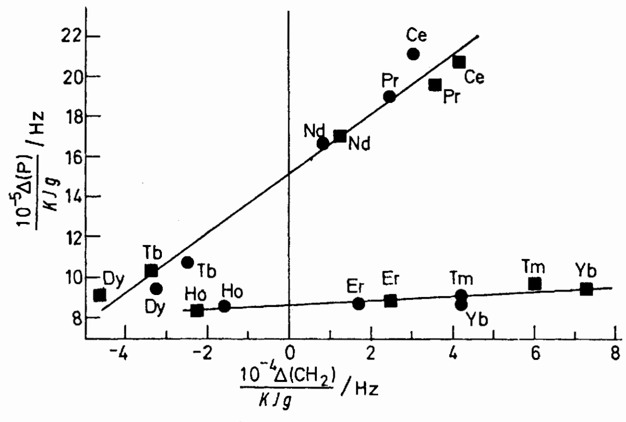

FIGURE 4 Plot of $\Delta(P)/KJg$ against $\Delta(CH_2)/KJg$. For details see Figure 3

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[9] C. D. Barry, J. A. Glasel, A. C. T. North, R. J. P. Williams, and A. V. Xavier, *Nature*, 1971, **232**, 236.

Theory section, the gradients of the straight lines in Figures 3 and 4 are functionally related to the geometrical quantities r and θ for the ^{31}P and ^{1}H nuclei in the complexes. It may be noted that the gradients in Figure 3 are greater than the corresponding ones in Figure 4. This effect can be attributed entirely to the fact that the CH_2 protons are closer to the lanthanoid nucleus than the CH_3 protons so the value of r_j in equation (4) is smaller for the methylene protons.

It is reasonable to assume that, independent of other motions within the complex, there is rapid averaging of the position of the methyl and methylene protons due to rotation about the C–C, C–O, and O–P bonds in solution. Since we see no evidence of the free ligand and since the chemical shifts of the lanthanum and lutetium complexes are nearly identical, we assume that there is no substantial change in the structure (such as a transition from eight- to six-co-ordination or complexation of the $[AsPh_4]^+$ counter ion) between Dy and Ho. The pseudo-contact shift of the methyl or methylene protons does not change drastically between the light and heavy lanthanoids; thus it is likely that the average positions of the protons is not very different. The large difference in the gradient for the light and heavy lanthanoids in Figures 3 and 4 must be due to a change in the average position of the ^{31}P nucleus. From this we conclude that the difference between the light and the heavy lanthanoids is not a simple change in ionic radius of the metal ion but is rather a change in geometry or perhaps a change in the fluxional geometries available due to the change in the Ln^{3+} radius. *X*-Ray powder patterns of the $[Ce\{S_2P(OEt)_2\}_4]^-$ and $[Er\{S_2P(OEt)_2\}_4]^-$ salts were measured to investigate the solid-state structures but no difference could be detected between the two powder patterns. This result simply indicates that the structure in the solid state is somewhat regulated by the packing and ionic forces in the crystal, whereas in solution the complexes are free to adopt whatever geometry is energetically most favourable. In the absence of more solution data it is impossible to draw more definite conclusions about the structures in solution. Finally, the fact that the ^{1}H and ^{31}P n.m.r. shifts are virtually identical for the complexes of La^{III} and Lu^{III} while Figures 3 and 4 imply a definite change in the structure of the complexes across the lanthanoid series simply serves to re-emphasize the fact that lanthanoid paramagnetic shifts can be powerful aids to detecting structural changes in solution.

The possibility of *f*-orbital participation in covalent bonding has been mentioned for years. The participation of actinoid *f* orbitals in bonding was suggested as early as 1950,[10] and Eisenstein discussed hybridization involving *f* orbitals especially with respect to uranium complexes.[11] The early work on lanthanoid shift reagents frequently involved the use of oversimplified models for the shift, but it was soon recognized that the contact interaction often made significant contributions to the total shift, especially of ^{13}C resonances.[12] Most investigations of lanthanoid shift reagents have tended to regard the contact shift as an undesirable nuisance in calculations of geometrical configurations in solution. LaLancette *et al.*[13] and Horrocks *et al.*[14] investigated the relative contact shifts of protons in σ- and η-bonded transition-metal complexes. They were able to draw conclusions about the delocalization of the paramagnetic electrons in complexes of Ni and Co. Our work is not amenable to the same kind of analysis because we do not have contact shifts for several nuclei within a single complex.

It is informative to compare the contact shifts obtained in this work with some of those available in other paramagnetic complexes. Reuben and Fiat[5] (in agreement with the results of Lewis *et al.*[7]) obtain values of 0.84—0.57 MHz for the scalar coupling constant between the lanthanoids and ^{17}O in $[Ln(OH_2)_9]^{3+}$ complexes. The Ln–^{17}O coupling constant is a one-bond coupling and so at first glance it might be expected to be larger than the Ln–^{31}P coupling reported in this work. Undoubtedly, the increased covalency in the dithiophosphate complexes is due to two effects: the bidentate nature of the ligand giving more paths for electron transfer; and, more importantly, the greater polarizability of sulphur than oxygen in the metal–ligand bond. The scalar coupling for cytidine-5′-monophosphate to lanthanoid ions can be calculated from the data of Dobson *et al.*[4] The average coupling constant from their data is 0.08 MHz which is further confirmation of the increase in covalency in going from metal–oxygen to metal–sulphur bonds.

Another interesting set of scalar couplings in *f*-electron systems are the values of the scalar coupling constant calculated by Streitweiser *et al.*[15] for uranium(IV) and neptunium(IV) tetramethylcyclo-octatetraene complexes. They reported proton–actinoid coupling constants between 1.02 and 0.52 MHz and attributed these to charge transfer from ligand molecular orbitals to vacant *f* orbitals. Single-bond scalar coupling constants have been measured for a number of transition-metal aqua-complexes. The values are normally between 5 and 50 MHz depending on the metal ion studied.[16] These values are certainly larger than the couplings in this study. The reasons for the greater scalar coupling constant in transition-metal-oxygen-17 bonds is due to the fact that they are one-bond couplings using *d* orbitals, and the overlap between ligand molecular orbitals and metal *d* orbitals is undoubtedly greater than the corresponding situation with metal *f* orbitals.

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[10] K. Street, jun., and G. T. Seaborg, *J. Amer. Chem. Soc.*, 1950, **72**, 2790.

[11] J. C. Eisenstein, *J. Chem. Phys.*, 1956, **25**, 142.

[12] O. A. Gansow, P. A. Loeffler, R. E. Davis, M. R. Willcott, III, and R. E. Lenkinski, *J. Amer. Chem. Soc.*, 1973, **95**, 3390.

[13] See, for example, E. A. LaLancette, D. R. Eaton, R. E. Benson, and W. D. Phillips, *J. Amer. Chem. Soc.*, 1962, **84**, 3968.

[14] W. D. Horrocks, jun., R. C. Taylor, and G. N. LaMar, *J. Amer. Chem. Soc.*, 1964, **86**, 3031.

[15] A. Streitweiser, jun., D. Dempf, G. N. LaMar, D. G. Karraker, and N. Edelstein, *J. Amer. Chem. Soc.*, 1971, **93**, 7343.

[16] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307; 1964, **41**, 2553.

A final comparison can be made with the e.s.r. results of Cavell *et al.*[17] who measured the hyperfine coupling constant for $^{31}P-V^{IV}$ in $[VO\{S_2P(OEt)_2\}_2]$, the vanadyl analogue of the lanthanoid complexes in this study. They reported a hyperfine coupling constant (converted into frequency units) of 142 MHz, two orders of magnitude larger than that found for the lanthanoids. This is a direct indication of the greatly enhanced covalency in transition-metal–ligand bonds due to the extension of the *d* orbitals beyond any shielding electronic orbitals.

In conclusion, chemical-shift measurements of different nuclides in a series of lanthanoid complexes can be an effective technique for separating contact and pseudo-contact shifts. The paramagnetic electrons act as chemical multipliers in a manner which may permit detection of rather subtle structural changes in solution. A qualitative comparison of the contact shift in $[Ln\{S_2P(OEt)_2\}_4]^-$ complexes with contact shifts in other metal ion–ligand complexes leads one to conclude that there is a covalent contribution to the lanthanoid–ligand bond. This contribution is greater for sulphur than for oxygen donors, and *f*-orbital participation in bond formation is orders of magnitude less than for *d* orbitals.

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[17] R. G. Cavell, E. D. Day, W. Byers, and P. M. Watkins, *Inorg. Chem.*, 1972, **11**, 1591.