A Paramagnetic Nuclear Magnetic Resonance Study of the Lanthanide Complexes $[Ln(S_2PMe_2)_4]^-$. Determination of Phosphorus Hyperfine Coupling and Solution Structures

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The complexes $[AsPh_4][Ln(S_2PMe_2)_4]$ have been prepared and their ^1H and ^{31}P n.m.r. spectra recorded at room temperature. The proton isotropic shifts are pseudo-contact in origin. The ^{31}P shifts contain both contact and pseudo-contact contributions. The method used to separate the two contributions is described and demonstrates a change in solution structure at Ln = Dy. The change in structure is associated with a reduction in the hyperfine coupling to phosphorus from 1.09 to 0.51 MHz. For the heavy ions the relative phosphorus pseudo-contact shift falls almost to zero (−2.4 *versus* 32.0). The results are consistent with a change in structure from dodecahedral to square-antiprismatic.

Our interest in the co-ordination chemistry of the *f* transition elements with non-oxygen donor ligands has led to the preparation and characterisation of a number of dithiophosphinate ($R_2PS_2^-$) complexes of the lanthanides and actinides.[1] The presence of the easily polarisable sulphur donor atoms allows one to suggest that any covalent interaction between the soft ligand and the hard metal ion should be enhanced relative to the more common oxygen donor systems. The dithiophosphinates also have the added advantage over other sulphur donor ligands, *e.g.* dithiocarbamates, of the presence of a convenient n.m.r. probe in the ^{31}P nucleus. Thus, one of the properties that we have chosen to study in order to characterise this type of bonding is the hyperfine coupling between the unpaired *f* electrons and the phosphorus nuclei.

When a hyperfine interaction exists, without being specific about the mechanism, we must postulate a covalent interaction to allow transmission of the electron-spin information from the metal ion to another nucleus. Having determined that such an interaction exists, it then becomes of interest to investigate the factors which determine its magnitude. The possibility of varying the substituents at phosphorus in compounds of the present type has led us to carry out a systematic study of dithiophosphinate complexes of the lanthanides. The results may also be compared with the *X*-ray crystal structures which have been determined in a parallel study.[1]

In a previous paper [2] we showed that the phosphorus hyperfine coupling may be obtained from the ^1H and ^{31}P n.m.r. spectra for the series of complexes $[Ln\{S_2P(OEt)_2\}_4]^-$. At the same time we were able to demonstrate a change in solution structure at Ln = Ho with a corresponding change in the hyperfine coupling constant. This structural change was recently shown to be most probably from a D_{2d} dodecahedron to a D_2 square antiprism.[3]

The hyperfine coupling is obtained from the measurement of the ^{31}P contact shifts,[4] and the structural information from the corresponding pseudo-contact shifts.[5,6] A simple treatment of the n.m.r. data to allow separation of the contact and pseudo-contact contributions to the total isotropic shifts was presented in our previous article.[2] In this paper we show that this method is a special case of a more general treatment, and apply it to the n.m.r. spectra of the title compounds.

The solid state structures of two members of the series are presented in the preceding paper [1] and compared with the present n.m.r. results.

Theory

The isotropic shift, Δ, is defined as the chemical shift difference between a nucleus in a paramagnetic complex and the same nucleus in a diamagnetic analogue. In the general case the total isotropic shift of nuclei in paramagnetic complexes is given by the sum of the Fermi contact (c) and pseudo-contact (pc) interactions, equation (1). The contact term is a scalar interaction, and the pseudo-contact interaction is dipolar in origin.

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

The contact shift may be written as equation (2) following the work of Golding and Halton,[4] where β is the Bohr magneton, *k* is the Bolzmann constant, *T* is the absolute temperature, γ is the gyromagnetic ratio of the observed nucleus, *A*/*h* is the hyperfine coupling in frequency units, and $\langle S_z \rangle$ is the projection of the total electron spin onto the *z* axis (direction of the external magnetic field).

$$\Delta_c = -\frac{2\pi\beta}{3kT\gamma}\cdot\langle S_z\rangle\cdot\frac{A}{h} \qquad (2)$$

If the magnetic susceptibility tensor is axial or effectively axial, the pseudo-contact shift may be written as equation (3) following Bleaney.[6] Here, *g* is the appropriate Landé *g* factor, *J* describes the ground state of the ion, D_z is the *z* component of the zero-field splitting tensor, *r* is the radius vector from the lanthanide ion to the observed nucleus, θ is the angle between *r* and the principal axis of the magnetic susceptibility tensor, and β, *k*, and *T* are as before. The axial approximation is considered to be valid for the present case as the molecules are fluxional. However, even if they were not fluxional, the most likely structures have axial symmetry (see below).

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

For any pair of nuclei *i* and *j* in the same complex only the geometrical part of equation (3) changes, hence it is convenient to define a ratio G_i/G_j equation (4), and eliminate the need to describe accurately the magnetic properties of the lanthanide ion.

$$\frac{G_i}{G_j} = \frac{(3\cos^2\theta_i - 1)r_j^3}{(3\cos^2\theta_j - 1)r_i^3} \qquad (4)$$

Table. Isotropic shift data [a] for $[Ln(S_2PMe_2)_4]^-$

Ln	Δ_t^P	Δ_t^H	$10^{-5}(\Delta_t^P/K\langle S_z\rangle)$ [b]	$10^{-3}(\Delta_t^H/K\langle S_z\rangle)$ [b]	Δ_c^P [c]	Δ_{pc}^P [d]
Ce	−62.6	−0.43	14.74	10.13	−48.9	−13.7
Pr	−164.5	−0.73	12.75	5.64	−141.3	−23.2
Nd	−213.6	−0.52	10.97	2.65	−197.1	−16.5
Tb	903.0	−20.05	6.54	−14.53	1 543.8	−640.8
Dy	701.7	−17.30	5.67	−13.97	660.4	41.3
Ho	510.9	−5.85	5.20	−5.95	496.9	14.0
Er	305.0	6.16	4.59	4.57	319.7	14.7
Tm	125.3	5.94	3.55	16.69	139.5	−14.2
Yb	67.1	2.00	5.97	17.86	72.0	−4.9

[a] In p.p.m. relative to the diamagnetic La analogue ($\delta_H = 3.72$ p.p.m. *versus* $SiMe_4$, $\delta_P = 51.6$ p.p.m. *versus* 85% H_3PO_4). [b] $K = -2\pi\beta 3/kT\gamma_p$. [c] Calculated from $\Delta_c^P = \Delta_t^P - \Delta_{pc}^P$. [d] Calculated from $\Delta_{pc}^P = \text{slope} \times \Delta_t^H$.

If we now rewrite equation (1) to give equation (5), substitute for Δ_{pc}^J [equation (6)], and insert equation (2) for the contact

$$\Delta_t^i = \Delta_c^i + \frac{G_i}{G_J}\Delta_{pc}^J \qquad (5)$$

$$\Delta_t^i = \Delta_c^i + \frac{G_i}{G_J}(\Delta_t^J - \Delta_c^J) \qquad (6)$$

terms, we obtain equation (7). The parameter Δ_t is observed

$$\Delta_t^i = - \frac{2\pi\beta}{3kT\gamma_i}\cdot\langle S_z\rangle\cdot\frac{A^i}{h} + \frac{G_i}{G_J}\left(\Delta_t^J + \frac{2\pi\beta}{3kT\gamma_J}\cdot\langle S_z\rangle\cdot\frac{A^J}{h}\right) \qquad (7)$$

and is nucleus and lanthanide dependent, γ is known and is nucleus dependent, $\langle S_z\rangle$ is known [4] and is ion dependent, $2\pi\beta/3kT$ is constant at constant temperature and known, and A/h and G are nucleus dependent and unknown.

Bearing in mind the inherent correlations in equation (7), if enough nuclei are observed and if one observed nucleus is not contact shifted ($A/h = 0$), *e.g.* a proton far from the lanthanide ion, then the equation may be solved for $n - 1$ values of A/h and the relative geometrical terms. For n nuclei there are thus n observed values of Δ_t, $n(n - 1)/2$ equations of type (7) and $2n - 2$ unknown. This treatment is general for any experiment concerning lanthanide induced shifts where the axial approximation is valid.

In the case where a whole series of complexes has been studied, if there is no structural change, and if A/h is constant from one ion to another as has been postulated for an isostructural series,[7,8] then, for m different ions, we may generate $m \times n(n - 1)/2$ equations of type (7) and may obtain a solution with less observed nuclei. These two different levels of sophistication both require the use of non-linear least-squares methods.

In the present case where only two nuclei have been observed, this treatment is not possible, however, if Δ_c^J is zero ($A^J/h = 0$), equation (7) may be rearranged to give the linear expression (8) for a series of isostructural complexes with a constant value of A/h. This equation is identical in form

$$\Delta_t^i \cdot - \left(\frac{3kT\gamma_i}{2\pi\beta\langle S_z\rangle}\right) = \frac{A^i}{h} + \frac{G_i}{G_J}\cdot\Delta_t^J\cdot\left(- \frac{3kT\gamma_i}{2\pi\beta\langle S_z\rangle}\right) \qquad (8)$$

to equation (7) of our previous article.[2] Clearly a plot of the left hand side of equation (8) against the same function of Δ_t^J will give a straight line of intercept A^i/h and slope G_i/G_J.

Experimental

The crystalline complexes $[AsPh_4][Ln(S_2PMe_2)_4]$ were prepared from the hydrated chlorides by a similar method to that used to prepare the $[PPh_4]^+$ analogues.[9] The heavier members of the series are extremely hygroscopic and difficult to isolate (Er—Yb). For this reason, these complexes were prepared from the anhydrous chlorides, all manipulations being carried out in dry solvents under argon by Schlenk techniques. All isolated complexes gave satisfactory elemental analyses (C, H, S, Ln).

Samples for n.m.r. investigation of the light members were prepared by the addition of CD_2Cl_2 (dried over 4 Å molecular sieves) to the crystalline salts. For the heavy ions, the samples were prepared by distilling CD_2Cl_2 from P_2O_5 onto the complexes under vacuum. The resulting solutions were *ca.* 2 : 1 in the paramagnetic complex and the diamagnetic lanthanum analogue as an internal reference for both ^1H and ^{31}P spectra. For those samples where the proton isotropic shifts were small, the lanthanum complex was omitted and the proton impurity in the solvent used as the internal reference. The ^1H and ^{31}P chemical shifts of the diamagnetic complex were measured relative to internal $SiMe_4$ and external 85% H_3PO_4.

The proton spectra were recorded on a Bruker WP-60 spectrometer at 60 MHz, and the ^{31}P spectra recorded without proton decoupling to eliminate temperature fluctuations with a Bruker HX-90 or CXP-200 spectrometer operating at 36.43 or 80.99 MHz respectively. All spectra were obtained at room temperature. The sweep width and repetition rate were varied depending on the chemical shifts and approximate relaxation rates.

Results and Discussion

Although the literature abounds with n.m.r. studies, of various degrees of sophistication, using lanthanide shift reagents to study organic substrates in rapid exchange,[10] the number of studies carried out on non-labile, well defined lanthanide complexes is relatively small. The absence of intermolecular ligand exchange in the present study was confirmed as in our previous paper.[2] This fact also allowed us to employ the diamagnetic lanthanum complex as an internal reference. The molecules are fluxional as expected for a co-ordination number of eight,[11] which means that, irrespective of any postulated structure, only one proton and one phosphorus resonance was observed.

All the spectra were recorded at ambient temperature (302 K) and the observed isotropic shifts relative to the diamagnetic lanthanum complex are reported in the Table. The ^{31}P spectra were not proton decoupled because for most samples the line

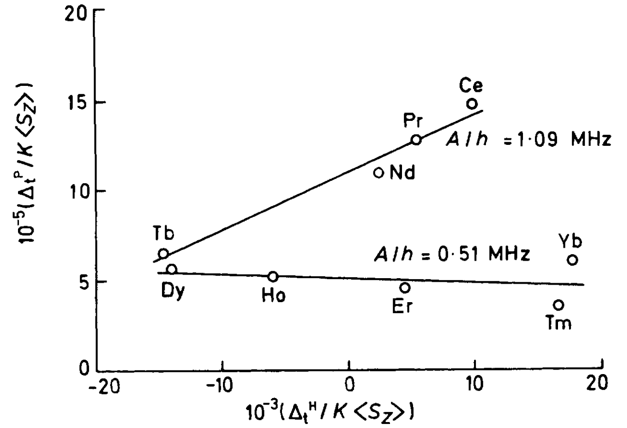

Figure 1. Plot of $\Delta_t^P/K\langle S_z\rangle$ against $\Delta_t^H/K\langle S_z\rangle$; $K = -2\pi\beta 3kT\gamma_P$

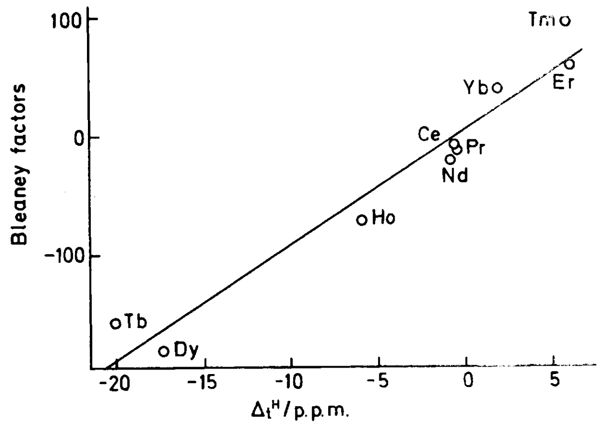

Figure 2. Plot of Δ_t^H against ' Bleaney factors '

broadening due to paramagnetic relaxation was greater than ^2J(HP) (12.0 Hz), and more importantly, to avoid heating of the sample especially in the high-field spectrometer. It is clear from the theoretical discussion above that we require all spectra to be obtained at the same temperature.

We have made the assumption that the proton shifts are purely pseudo-contact in origin and that the axial approximation is valid. These assumptions are justified below. The observed ^{1}H and ^{31}P isotropic shifts have been divided by the appropriate constants and plotted according to equation (8) in Figure 1. It is clear that there are two distinct straight lines, the upper corresponding to the light ions and the lower to the heavy ones. The observed slopes corresponding to the ^{31}P dipolar shift relative to the ^{1}H total shift are 32.0 and -2.4, *i.e.* the phosphorus shift for the heavy ions has a much smaller dipolar component than for the light ions. The ^{31}P hyperfine coupling constants obtained from the intercepts are 1.09 and 0.51 MHz for the light and heavy ions respectively.

Clearly we are observing a change in solution structure at dysprosium. This is a similar observation to that made for the series $[\mathrm{Ln\{S_2P(OEt)_2\}_4}]^-$ where the change in structure occurred at holmium.[2] In the solid state, neither of these series of complexes changes molecular geometry.[1,3] For the present compounds the co-ordination polyhedron is the D_{2d} dodecahedron distorted towards the D_2 square antiprism. In the ethoxy compounds the structure is an almost perfect D_{2d} dodecahedron. It is postulated that the structures in solution are the dodecahedron for the light ions and the square antiprism for the heavy ones. The arguments for this have already been presented.[1,3] If these geometries are correct we would expect the magnetic susceptibility tensor to be axially symmetric.

It is of interest that the magnitude of the hyperfine coupling is sensitive to the change in geometry, changing by a factor of two. This phenomenon was previously observed for the ethoxy series, and has since been observed for analogous series where the substituents at phosphorus are OMe and OPr^i.[12] This means that we are observing a 4*f* electron property that has directional dependence. As we have previously shown that the 4*f* orbitals themselves do not directly enter into the bonding scheme,[13] there must be a preferred interaction between the electronic ground state and excited state configurations derived from the orbitals used in the bonding in the dodecahedron, rather than in the square antiprism. This is a purely qualitative argument as we do not have enough information to quantify it as yet. However, the utilisation of the 6*s* orbital alone as previously postulated [7] is not sufficient as this would preclude a geometrical dependence.

A further observation is that the alkyl substituent (Me) at phosphorus tends to decrease the value of the hyperfine coupling compared to alkoxy substituents. The values of 1.52 and 0.86, and 1.60 and 0.85 MHz, were observed with the substituents OEt,[2] and OPr^i,[12] respectively compared to 1.09 and 0.51 MHz observed here. This is in accord with Bent's rules [14] concerning the *s* character of the bonds. More *s* character would be expected in the P–S bonds when the other substituents are electron withdrawing, and thus the contact interaction would be increased.

One of the points of interest in spectra of this type is the origin of the observed isotropic shifts. As this point is invariably discussed in papers concerning lanthanide shift reagents, we would like to point out the dangers of certain of the methods employed to determine whether an observed shift is pseudo-contact (dipolar) or contact (scalar) in origin, and whether a series of compounds may be considered isostructural.

If we rewrite equation (3) in its full form as given by Bleaney,[6] equation (9), we see the additional terms A_2^0 from

$$\Delta_{pc} = \frac{g^2\beta^2(3\cos^2\theta - 1)}{60(kT)^2r^3} \times (2A_2^0)\langle r^2\rangle J(J+1)(2J-1)(2J+3)\langle J||\alpha||J\rangle \quad (9)$$

the crystal field expansion, $\langle r^2\rangle$, the expectation value of the radius of a 4*f* orbital, and the reduced matrix element $\langle J||\alpha|J\rangle$ which is a number. In an isostructural series, the only part of this expression that is ion dependent is $g^2J(J+1)(2J-1)(2J+3)\langle J||\alpha||J\rangle$. These values are the so-called ' Bleaney factors' and are tabulated.[6] The isotropic shifts of a nucleus in an isostructural series of compounds plotted against the relevant ' Bleaney factors ' should give a straight line if the shifts are dipolar in origin. The obtention of a straight line is, however, no guarantee of an isostructural series. In Figure 2 we have carried out this type of plot for the methyl resonances in the present study, and the result is quite a reasonable straight line although we know that this is not an isostructural series. We were led into drawing such an erroneous conclusion in the first report [9] of the complexes $[\mathrm{Ln\{S_2P(OEt)_2\}_4}]^-$, a conclusion which we corrected when the complete analysis was carried out.[2] The only conclusion that we can draw from Figure 2 is that the proton geometrical factor, averaged by intramolecular exchange, is about the same in both structures, and that the observed shifts are probably purely dipolar in origin.

Two other tests for an isostructural series have been proposed which are essentially the same. As shown above, the

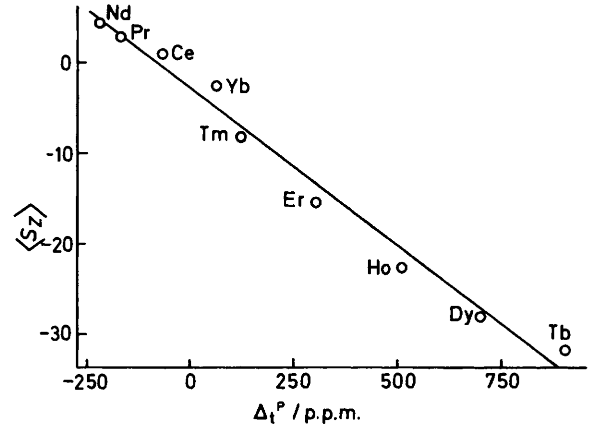

Figure 3. Plot of Δ_t^P against $\langle S_z \rangle$

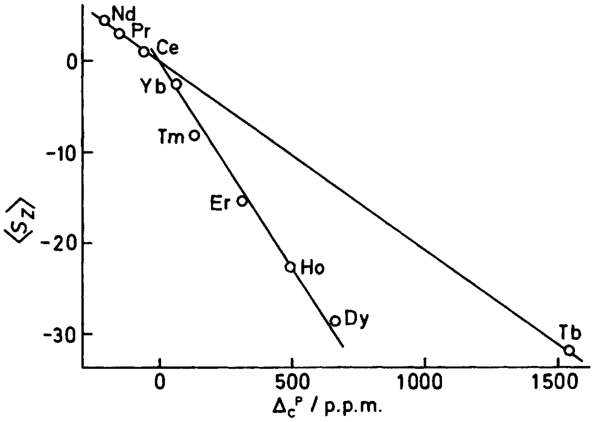

Figure 4. Plot of Δ_c^P against $\langle S_z \rangle$, Δ_c^P being derived from Δ_t^P − (slope × Δ_t^H)

ratio of two dipolar shifts should be independent of the lanthanide ion. This may be calculated as a ratio for each ion [15] or the shift of one plotted against the other to give a straight line.[16] In the present case we do not have two nuclei shifted by a purely dipolar mechanism, however, in the study where the ligand was $(EtO)_2PS_2^-$ this situation existed. Clearly, if plots of the observed shifts against the 'Bleaney factors' gave straight lines, the ratio of the shifts must be a constant and one plotted against the other necessarily gives a straight line. Again the erroneous conclusion of an isostructural series would be reached.

The other extreme would be the observation of a purely contact shift. This being the case, a plot of the observed shift against the appropriate value of $\langle S_z \rangle$ would give a straight line for an isostructural series with no variation in the hyperfine coupling.[4,7,8] It was recently pointed out to us [16] that a plot of this type with our previously published ^{31}P data [2] suggest that these shifts are purely contact in origin and that the complexes are isostructural.

In Figure 3 we present the data from the present study and obtain a 'straight line.' However, the conclusion that the ^{31}P shifts are purely contact in origin and that the complexes form an isostructural series is erroneous. In Figure 4 we show the analogous plots for the derived phosphorus contact shifts after correcting for the pseudo-contact contribution. These values are also reported in the Table. Now it is again clear that there are two straight lines, a structural change having taken place at dysprosium. As shown above, the ^{31}P dipolar shift for the heavy ions is quite small, hence there is little difference between Figures 3 and 4 in this region. The ion that really determines that there are two straight lines and not one is terbium.

It is perhaps pertinent to make a few remarks about the method we have chosen to separate the contact and pseudo-contact contributions to the total shifts. It is clear that this is not a new problem and that other methods have been proposed for carrying out this operation.[15,17,18] However, most methods require that an isostructural series exist and that the hyperfine coupling be constant throughout the series. This is not the case with our method if enough information is available to permit use of the general equation (7) for one ion. The use of ratios in the way we have derived the equations effectively expands the data set from n chemical shifts to $n(n - 1)/2$ independent observations. Most other methods also require the use of the 'Bleaney factors' which we have eliminated. This is a desirable facet of this work as the values given by Bleaney have been criticised [19] and may be up to 20% in error. Our method also seems to be especially sensitive in detecting structural changes in solution.

We have thus shown that for the complexes $[Ln(S_2PMe_2)_4]^-$ there is a change in structure at dysprosium (probably from dodecahedral to square-antiprismatic) and that the hyperfine coupling to phosphorus is sensitive to structural parameters as well as to the substituents at phosphorus. At the same time we have shown that there are dangers in some of the common ways of analysing lanthanide induced shift data.

Acknowledgements

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