A Paramagnetic Nuclear Magnetic Resonance Study of the Lanthanide Complexes $[Ln(S_2PR_2)_4]^-$, R = OMe, OPr^i. Determination of Phosphorus Hyperfine Coupling and Solution Structures

STAVROS SPILIADIS and A. ALAN PINKERTON

Institut de chimie minérale et analytique, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland

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The ^1H and ^{31}P NMR spectra of the complexes $[AsPh_4][Ln(S_2PR_2)_4]$ for R = OMe, OPr^i have been recorded at room temperature. The proton isotropic shifts are pseudocontact in origin. The total ^{31}P isotropic shifts have been factored into their contact and pseudocontact contributions. The method used to separate the contact and pseudocontact shifts demonstrates a change in solution structure at Ln = Ho. The change in structure is associated with a reduction in the hyperfine coupling to phosphorus from 1.68 to 0.82 MHz (OMe), and from 1.57 to 0.85 MHz (OPr^i). The relative phosphorus pseudocontact shift falls from 31.7 for the light ions to 3.0 for the heavy ones (OMe), from 16.4 to 0.55 (OPr^i–CH) and from 57.1 to 1.84 (OPr^i–CH_3). These results are consistent with a change in structure of the coordination polyhedron from dodecahedral to square antiprismatic.

Introduction

Our interest in the coordination chemistry of the *f* transition elements with soft donor ligands has led to the preparation and characterisation of a number of dithiophosphinate, $R_2PS_2^-$, complexes of the lanthanides and actinides [1]. Clearly any covalent interaction between a soft, easily polarisable ligand and a hard metal ion should be enhanced relative to the more common oxygen donor systems. The presence of a convenient NMR probe in the ^{31}P nucleus of the dithiophosphinates is a particular advantage of these ligands over other common sulphur donors *e.g.* dithiocarbamates. 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 of the paramagnetic ions and the phosphorus nuclei.

The existence of a hyperfine interaction requires the presence of a covalent interaction to allow transmission of the electron spin information from the metal ion to a ligand nucleus. If such an interaction exists, the study of the factors which determine its magnitude then becomes important and should eventually lead to a good theoretical model to explain the phenomenon. The possibility of varying the steric and electronic properties of 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 previous reports we showed that the phosphorus hyperfine coupling may be obtained from the ^1H and ^{31}P NMR spectra for complexes of the type $[Ln\{S_2PR_2\}_4]^-$ for R = Me [2] and OEt [3]. At the same time we demonstrated a change in solution structure at Ln = Dy(Me) or Ho(OEt) with a corresponding change in the hyperfine coupling constant. This structural change was interpreted to be most probably from a D_{2d} dodecahedron to a D_2 square antiprism in both cases [4, 5].

The magnitude of the hyperfine coupling is obtained from the measurement of the ^{31}P contact shifts, and the structural information from the corresponding pseudocontact shifts. The separation of the contact and pseudocontact contributions to the total isotropic shifts may be obtained from a simple treatment of the NMR data and the details of this type of analysis have already been published [2, 3].

In this paper we apply the same treatment to the complexes $[Ln(S_2PR_2)_4]^-$ where R = OMe and OPr^i, and compare the results with those obtained for similar compounds with R = Me and OEt and with the solid state crystal structures reported in the preceding paper.

Experimental

The crystalline complexes $[AsPh_4][Ln(S_2PR_2)_4]$, R = OMe, OPr^i, were prepared as described previously [1]. Samples for NMR investigations of the light members were prepared by the addition of CD_2Cl_2 (dried over 4 Å molecular sieves) to the crystalline

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salts. For the heavy ions for which the complexes tend to be increasingly hygroscopic, the samples were prepared by distilling CD_2Cl_2 from P_2O_5 onto the complexes under vacuum. For Ln = Yb and R = OMe the complex rapidly decomposes, hence it was extracted from the reaction mixture with CD_2Cl_2 and used to obtain the NMR spectra before the yellow colour faded. 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 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

The number of paramagnetic NMR studies carried out on non-labile, well-defined lanthanide complexes is still relatively small. However, we have demonstrated that this technique can give valuable information concerning the bonding and the geometry of these complexes in solution [2–5]. The absence of intermolecular ligand exchange in the present study was confirmed as previously [3], and this fact allows us to employ the diamagnetic lanthanum analogues as an internal reference. The molecules are fluxional as expected for a coordination number of eight [6]. This means that irrespective of any postulated structure, only one (OMe) or two (OPr^i) protons and one phosphorus resonance were 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 Tables I and II. The ^{31}P spectra were not proton decoupled because for most samples the line broadening due to paramagnetic relaxation was greater than the phosphorus–proton J coupling and, more importantly, to avoid heating of the sample especially in the high field spectrometer. It is clear from the theoretical discussion that follows that we require all spectra to be obtained at the same temperature.

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 and pseudocontact interactions, eqn. (1):

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

The contact term is a scalar interaction, and the pseudocontact interaction is dipolar in origin. We have recently shown [2, 3] that for a pair of nuclei (i, j) in the same complex, we may express the observed shifts as a function of one another as eqn. 2, if nucleus j is not contact shifted (*e.g.* a proton well removed from the paramagnetic center).

$$\Delta_t^i \cdot \frac{-3kT\gamma^i}{2\pi\beta\langle S_z\rangle} = \frac{A^i}{h} + \frac{G^i}{G^j} \cdot \Delta_t^j \cdot \frac{-3kT\gamma^i}{2\pi\beta\langle S_z\rangle} \qquad (2)$$

β is the Bohr magneton, k is the Bolzmann constant, T is the absolute temperature, γ^i is the gyromagnetic ratio of the observed nucleus i, A/h is the hyperfine coupling in frequency units, $\langle S_z\rangle$ is the projection of the total electron spin onto the z axis (direction of the external magnetic field), and G^i and G^j are the corresponding values of $(3\cos^2\theta - 1)/r^3$ for nuclei i and j (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).

TABLE I. Isotropic Shift Data for $[AsPh_4][Ln\{S_2P(OMe)_2\}_4]$.*

Ln	Δ_t^P	Δ_t^H	$\Delta_t^P/K\langle S_z\rangle$	$\Delta_t^H/K\langle S_z\rangle$	Δ_c^P	Δ_{pc}^P
Ce	−104.0	−0.93	24.50×10^5	21.90×10^3	−74.5	−29.5
Pr	−254.9	−1.19	19.80×10^5	9.23×10^3	−217.2	−37.7
Nd	−333.0	−0.94	17.10×10^5	4.83×10^3	−303.2	−29.8
Tb	1375.0	−28.86	9.96×10^5	-20.90×10^3	2289.9	−914.9
Dy	1099.7	−33.19	8.88×10^5	-26.80×10^3	2151.8	−1052.1
Ho	790.0	−13.23	8.05×10^5	-13.48×10^3	830.0	−40.0
Er	535.0	9.93	8.02×10^5	14.89×10^3	505.0	30.0
Tm	306.0	16.20	8.59×10^5	45.50×10^3	257.1	48.9
Yb	56.0	4.60	10.9×10^5	40.99×10^3	42.1	13.9

*$K = -2\pi\beta/3kT\gamma_P$.

TABLE II. Isotropic Shift Data for $[AsPh_4][Ln\{S_2P(OPr^i)_2\}_4]$.*

Ln	Δ_t^P	Δ_t^{CH}	$\Delta_t^{CH_3}$	$\Delta_t^P/K\langle S_z\rangle$	$\Delta_t^{CH}/K\langle S_z\rangle$	$\Delta_t^{CH_3}/K\langle S_z\rangle$	Δ_c^P	Δ_{pc}^P
Ce	−99.0	−1.89	−0.52	23.31×10^5	4.46×10^4	12.29×10^3	−68.6	−30.4
Pr	−243.2	−2.48	−0.68	18.86×10^5	1.92×10^4	5.26×10^3	−203.5	−39.7
Nd	−334.0	−2.46	−0.67	17.15×10^5	1.27×10^4	3.42×10^3	−294.7	−39.3
Tb	1413.0	−43.90	−13.10	10.24×10^5	-3.18×10^4	-9.49×10^3	2147.0	−734.0
Dy	1121.4	−52.67	−15.56	9.06×10^5	-4.25×10^4	-12.57×10^3	1997.6	−876.2
Ho	825.0	−21.16	−6.61	8.40×10^5	-2.30×10^4	-6.74×10^3	836.9	−11.9
Er	571.5	15.13	4.29	8.57×10^5	2.27×10^4	6.39×10^3	562.9	8.6
Tm	321.0	23.60	9.19	9.01×10^5	6.63×10^4	25.81×10^3	306.1	14.9
Yb	98.8	8.17	2.08	8.80×10^5	7.28×10^4	18.53×10^3	94.6	4.2

*$K = -2\pi\beta/3kT\gamma_P$.

For a series of isostructural complexes with a constant value of A/h this is a linear equation and a plot of $\Delta_t^i\cdot(-3kT\gamma^i/2\pi\beta\langle S_z\rangle)$ against the same function of Δ_t^j will give a straight line of intercept A^i/h and slope G^i/G^j. In developing eqn. 2 we made the assumption that the proton shifts in these complexes are purely pseudo-contact in origin and that the axial approximation is valid. The assumptions are justified below.

The observed ^1H and ^{31}P isotropic shifts have been divided by the appropriate constants and plotted according to eqn. 2 in Fig. 1 (OMe), 2(OPr^i-CH_3) and 3(OPr^i-CH). In all cases 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 ^1H total shift are 31.7 and 3.0 (OMe), 16.4 and 0.55 (OPr^i-CH) and 57.1 and 1.84 (OPr^i-CH_3) *i.e.* the phosphorus shift for the heavy ions has a much smaller dipolar component than for the light ions in both cases. The ^{31}P hyperfine coupling constants obtained from the intercepts are 1.68 and 0.82 (OMe), and 1.57 and 0.85 MHz (OPr^i) for the light and heavy ions respectively.

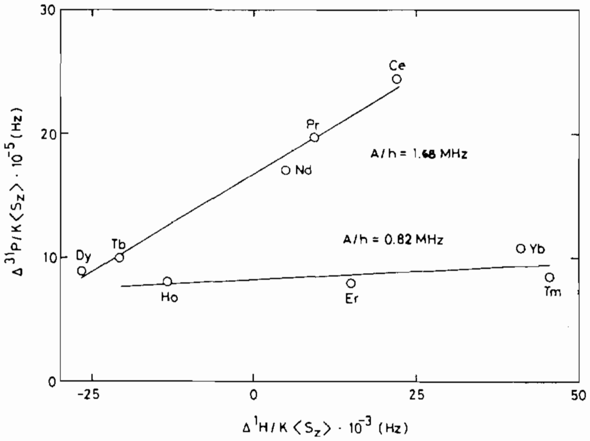

Fig. 1. Plot of $\Delta(P)/K\langle S_z\rangle$ against $\Delta(Me)/K\langle S_z\rangle$ where $K = (-2\pi\beta/3kT\gamma_P)$ for $[Ln\{S_2P(OMe)_2\}_4]^-$.

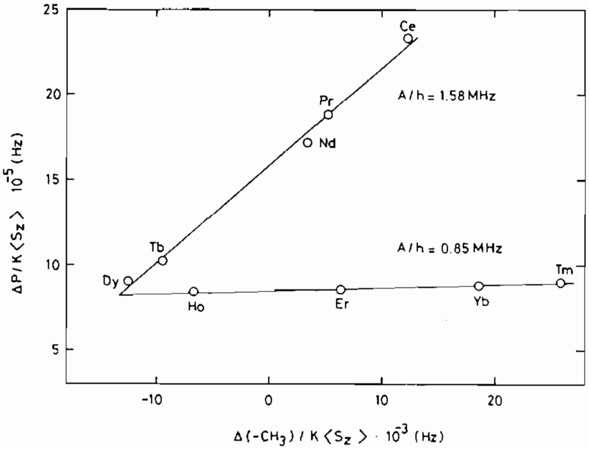

Fig. 2. Plot of $\Delta(P)/K\langle S_z\rangle$ against $\Delta(Me)/K\langle S_z\rangle$ where $K = (-2\pi\beta/3kT\gamma_P)$ for $[Ln\{S_2P(OPr^i)_2\}_4]^-$.

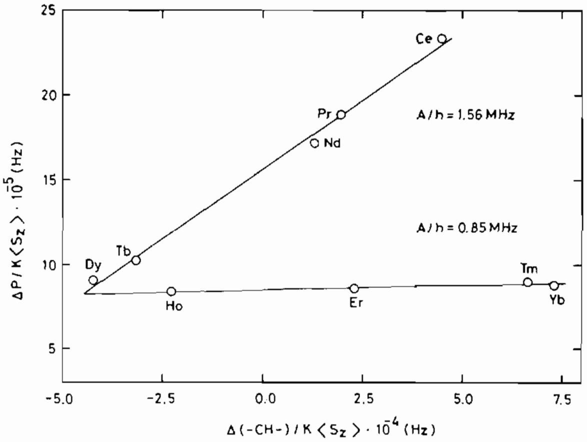

Fig. 3. Plot of $\Delta(P)/K\langle S_z\rangle$ against $\Delta(CH)/K\langle S_z\rangle$ where $K = (-2\pi\beta/3kT\gamma_P)$ for $[Ln\{S_2P(OPr^i)_2\}_4]^-$.

As we have observed in previous studies of this type there is a change in solution structure at holmium [2,3]. We have shown that neither of these series of complexes changes molecular geometry in the solid state [1]. For the present compounds the coordination polyhedron in the crystal is the D_{2d} dodecahedron with very little distortion, as was also observed for R = OEt [5]. It is postulated that the structures in solution are the dodecahedron for the light ions and the square antiprism for the heavy ones (see below).

The fact that the hyperfine coupling changes by a factor of two when the geometry of the polyhedron changes means that we are observing a 4*f* electron property that has directional dependence. It was previously shown that the 4*f* orbitals themselves do not directly enter into the bonding scheme, but that the ground state of the lanthanide ions contains a small contribution from excited states [7]. Thus 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; however, we hope to be able to confirm this conclusion by theoretical calculations which are at present incomplete.

When comparing the values of the hyperfine coupling reported here with those obtained in previous studies it appears that alkyl substituents at phosphorus tend to decrease the value of the hyperfine coupling compared to alkoxy substituents. The values of 1.68 and 0.82, 1.52 and 0.86, and 1.57 and 0.85 are observed for the substituents, OMe, OEt [3], OPr^i, respectively whereas for the methyl analogues [2], the smaller values of 1.09 and 0.51 MHz were observed. This is in accord with Bent's rules [8] 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.

An area of concern in the NMR spectra of paramagnetic lanthanide systems is the origin of the observed isotropic shifts and also whether the complexes belong to an iso-structural series. We would thus like to point out the dangers of certain of the methods employed to determine whether an observed shift is pseudocontact (dipolar) or contact (scalar) in origin, and whether a series may be considered to be isostructural.

If we write the equation for the pseudocontact shift in its full form as given by Bleaney [9], eqn. 3, we see, in addition to

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

the symbols already defined, the terms A_2^0 from 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 $g^2J(J+1)(2J-1)(2J+3)\langle J\|\alpha\|J\rangle$ which are the so-called 'Bleaney factors' whose values are tabulated [9]. Thus, for a nucleus in an iso-structural series of compounds, a plot of the observed isotropic shifts against the relevant 'Bleaney factors' should give a straight line if the shifts are dipolar in origin. However, obtaining a straight line is no guarantee of an isostructural series. In Fig. 4 we have carried out this type of plot for all the proton resonances in the present study, and the result in each case is quite a reasonable straight line although we know that this is not an iso-structural series. We were led into drawing such an erroneous conclusion in the first report of the complexes $[Ln\{S_2P(OEt)_2\}_4]^-$ [10], a conclusion which we corrected when the complete analysis was carried out [3]. A similar result was obtained for the methyl substituted analogues [2]. The only conclusion that we can draw from this figure 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.

The other extreme would be the observation of a purely contact shift. This is only likely to be the case when θ is fortuitously equal to 54.7°. In such a 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 if the hyperfine coupling remains constant [11, 12]. As it was pointed out to us [13] that a plot of this type with our previously published ^{31}P data for the OEt substituted complexes [3] suggested that these shifts were purely contact in origin and that the complexes were iso-structural, we carefully reanalysed the data, and also that of the Me substituted analogues, and demonstrated that the conclusion was erroneous [2].

In Fig. 5 we have plotted the data from the present study in this way and obtain 'straight lines'. However, we know that the ^{31}P shifts are not purely

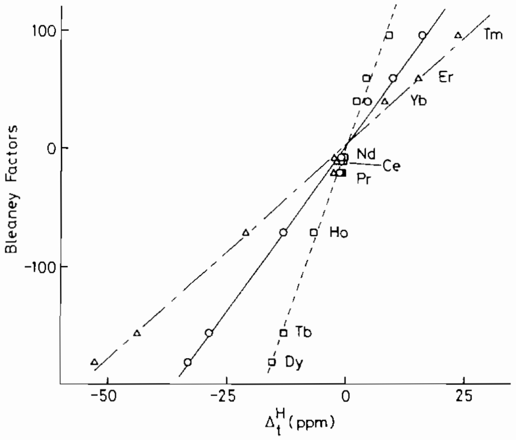

Fig. 4. Plot of Δ_t^H against 'Bleaney Factors', for $[Ln\{S_2PR_2\}_4]^-$. ○, R = OMe; △, R = $OPr^i(CH)$; □, R = $OPr^i(CH_3)$.

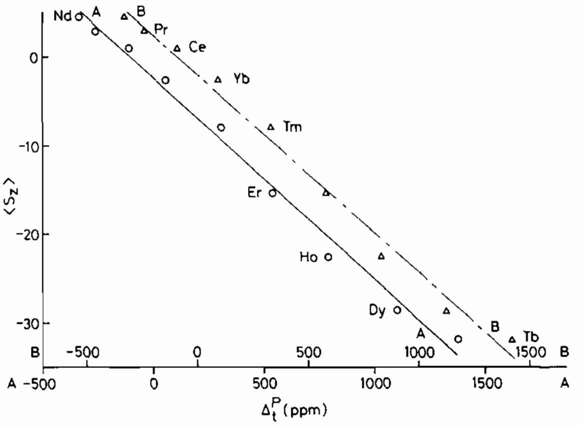

Fig. 5. Plot of Δ_t^P against $\langle S_z \rangle$, for $[Ln\{S_2PR_2\}_4]^-$, ○, R = OMe; □, R = OPr^i. The scales of the two plots are offset by 200 ppm for clarity.

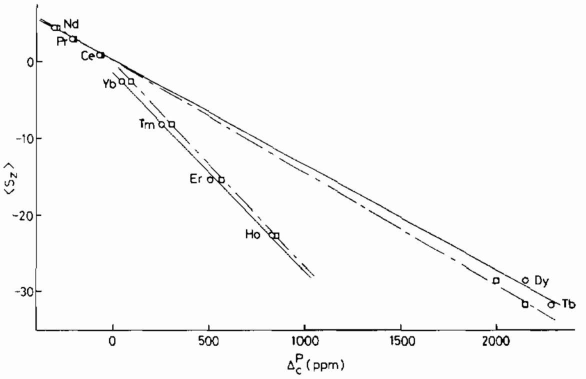

Fig. 6. Plot of Δ_c^P against $\langle S_z \rangle$, Δ_c^P being derived from Δ_t^P – (slope × Δ_t^H) for $[Ln\{S_2R_2\}_4]^-$, ○, R = OMe; △, R = OPr^i. For the latter the values derived from CH and CH_3 are averaged.

contact in origin and that the complexes do not form an iso-structural series. In Fig. 6 we show the analogous plots for the derived phosphorus contact shifts after correction for the pseudocontact contribution, and these values are also reported in Tables I and II. It is again clear that each series of complexes gives two straight lines and that a structural change has taken place at holmium.

As stated briefly above, we believe that the structural change is from a dodecahedron to a square antiprism. As the arguments for this conclusion have been developed in previous [4, 5] studies (R = Me, OEt) we will only present the main points here. The reasoning is based on the fact that the ^{31}P dipolar shift relative to a proton shift (the slope of the lines in Fig. 1–3) is always higher for the light ions than for the heavy ones. This means that the ^{31}P dipolar shift decreases in the same way because we know that the average proton positions observed for these fluxional molecules are fortuitously similar for both the heavy and light ions. This is why the plots of their isotropic shifts against the so-called 'Bleaney factors' (Fig. 4) give straight lines.

The dipolar shift in the axial approximation is a function of the complex geometry (eqn. 3). Thus the ^{31}P dipolar shift is proportional to $(3\cos^2\theta - 1)r^{-3}$ where r is the radius vector from the paramagnetic ion to the phosphorus nucleus, and θ is the angle between the vector r and the principal axis of the magnetic susceptibility tensor. This axis is taken to be collinear with the main symmetry axis of the molecule. Taking into account the lanthanide contraction and the minor changes possible in the ligand geometry, it is clear that r cannot vary enough to account for a sudden change of an order of magnitude in the phosphorus dipolar shift. We must thus turn our attention to possible variations in the angle between the vector r and the principal symmetry axis.

As presented in a previous article [5], there is an inherent difference between a D_{2d} dodecahedron and the D_2 square antiprism derived from it. The transformation is a low energy process which involves small rotations about the ligand two-fold axis. This transformation makes no change in the phosphorus position (therefore r does not change) and only minor changes in the sulphur positions. However, the main symmetry axis is flipped through an angle of 90°, thus there exists the potential for a change in the angle θ.

In Table III we present the angle θ observed between the vector r and the four-fold inversion axis for a number of structures of complexes of the present type and the related value of $(3\cos^2\theta - 1)$. On the basis of these predominantly dodecahedral structures we have calculated the value of θ that would be obtained between r and the pseudo-eight-fold inversion axis if these molecules were transformed into the corresponding square antiprism by the simple rotation mechanism described above. These values are also reported in Table III with their corresponding values of $(3\cos^2\theta - 1)$. Finally the observed limits to these parameters are reported. The values are calculated from all the structures of the type M(bidentate)$_4$ reported as dodecahedral or square antiprismatic in a review by Drew [14]. In this calculation we have made the assumption that the chelates are all planar. From this we may affirm that dodecahedral structures of the present type would be expected to have large ^{31}P dipolar shifts, whereas their square antiprismatic analogues should have small or zero ^{31}P dipolar shifts.

Although we have no proof that the two ideal structures exist in solution, the values obtained for θ from the crystallographic study coupled with the NMR results strongly suggest that these are the two most likely structures in solution. Further support for this conclusion comes from the calculations of Blight and Kepert [15]. As presented in the preceeding paper, the expected polyhedra are the D_{2d}

TABLE III. Angles (°) between the Ln–P Vector and the Principal Symmetry Axis for $[Ln(S_2PR_2)_4]^-$ and Values of $(3\cos^2\theta - 1)$.

Compound		Dodecahedron		Square antiprism		Ref.
Ln	R	θ	$3\cos^2\theta - 1$	θ	$3\cos^2\theta - 1$	
Ce	OMe	67.5	−0.56	49.8	0.25	[1]
Er	OMe	68.2	−0.59	49.7	0.26	[1]
Nd	OPr^i	67.5	−0.56	50.1	0.23	[1]
Ho	OPr^i	68.0	−0.58	51.6	0.16	[1]
Ce	Me	69.8	−0.64	53.8	0.05	[4]
Pr	Me	68.9	−0.61	54.0	0.04	[16]
Tm	Me	68.8	−0.61	53.6	0.06	[4]
La	OEt	66.8	−0.53	51.5	0.16	[5]
Er	OEt	67.6	−0.56	51.5	0.16	[5]
$M(L-L)_4$	min	66.1	−0.51	54.7	0.00	[14]
	max	73.1	−0.75	57.4	−0.13	

dodecahedron or the D_2 square antiprism. As the ionic radius decreases due to the lanthanide contraction, the normalised bite increases, hence the antiprismatic geometry becomes more likely.

We have thus shown that for the complexes $[Ln(S_2PR_2)_4]^-$ for R = OMe and OPr^i there is a change in solution structure at holmium (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.

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