Crystal and Molecular Structures† of $[AsPh_4][Ln(S_2PMe_2)_4]$ (Ln = Ce or Tm) and their Comparison with Results obtained from Paramagnetic Nuclear Magnetic Resonance Data in Solution

Stavros Spiliadis and A. Alan Pinkerton,*
Institut de Chimie Minérale et Analytique, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland
Dieter Schwarzenbach
Institut de Cristallographie, Université de Lausanne, Bâtiment des Sciences Physiques, Dorigny, CH-1015 Lausanne, Switzerland

The crystal structures of the title compounds have been determined from diffractometer data. The crystals of the cerium compound are tetragonal, space group $P4_222$ with four molecules in the unit cell of dimensions a = 11.461(2), c = 33.479(6) Å (R = 0.060). The thulium analogue is orthorhombic, space group $Pca2_1$ with four molecules in the unit cell of dimensions a = 19.899(3), b = 11.451(2), c = 19.051(2) Å (R = 0.037). In both compounds the lanthanide ion is co-ordinated to eight sulphur atoms with average Ln–S distances of 2.991 Å (Ce) and 2.870 Å (Tm). The co-ordination polyhedra are D_{2d} dodecahedra (*mmmm* isomer) distorted towards the D_2 square antiprism, the cerium compound having two independent molecules in the unit cell, both with 222 crystallographic symmetry. Despite the difference in crystallography between the Ce and Tm compounds, the molecular structures are quite similar in the solid state. However, in solution this is not the case as shown by paramagnetic n.m.r. data. The ^{31}P dipolar shifts are shown to be in accord with a change from dodecahedral to square-antiprismatic geometry when Ln = Dy.

Over the past few years we have prepared and characterised a number of dithiophosphinate ($R_2PS_2^-$) complexes of the f transition elements.[1–9] Our interests lie in the information available concerning covalency in these systems due to the soft polarisable character of the sulphur donor atoms, and the factors which determine their structures. The property that we have chosen to study as a measure of the covalent interaction is the hyperfine coupling of the unpaired electrons on the metal ion to the phosphorus nuclei in the dithiophosphinate ligands. This information is obtained from the n.m.r. spectra of the paramagnetic complexes which also yield structural information on the solution species. In our first study of this type on the series $[Ln(S_2PR_2)_4]^-$ (R = OEt), we demonstrated a change in solution structure where Ln = Ho from dodecahedral to square-antiprismatic, whereas the solid state structures are all dodecahedral.[5,9]

Wishing to determine the influence of the substituents at phosphorus on the magnitude of the hyperfine coupling and on the structure, as well as to gain some insight into the effect of structural changes on the hyperfine coupling, we have carried out a systematic study varying R.

Although we have previously reported the structure of $[Pr(S_2PMe_2)_4]^-$ as its $[PPh_4]^+$ salt,[1] it was clear that the first complexes prepared for the n.m.r. study [10] with $[AsPh_4]^+$ as the counter ion were not isomorphous, hence the structure of the cerium compound was determined in order to obtain information regarding the possible deformations caused by crystal packing. The thulium analogue was found to be isomorphous with the previously reported praseodymium structure,[1] and was determined to obtain information on the effect of changing the ionic radius of the metal.

In this paper we present the solid state structures of the two title compounds and compare them with the results obtained from the n.m.r. experiments which are reported in the following paper.[10]

Experimental

The complexes $[AsPh_4][Ln(S_2PMe_2)_4]$ (Ln = Ce or Tm) were prepared by a method similar to that used for the $[PPh_4]^+$ salts.[1,4] Suitable crystals for X-ray studies were obtained from ethanol (Ce) or isopropyl alcohol–CH_2Cl_2 (Tm) solutions. The cerium compound is stable in air and required no special precautions. The thulium analogue is very moisture sensitive and was handled in a dry atmosphere. The crystal (Tm) used for X-ray measurements was thus mounted under dry argon in a sealed glass capillary.

X-Ray Measurements and Structure Determination.—X-Ray intensity measurements were carried out with a Syntex $P2_1$ automatic four-circle diffractometer, backgrounds being obtained from analysis of the scan-profile,[11] and a numerical absorption correction applied as reported previously.[7] Crystal data, measurement methods, structure solution, and refinement are summarised in Table 1. Scattering factors for the neutral atoms were taken from Cromer and Mann,[12] and anomalous scattering coefficients from Cromer and Liberman.[13] Computer programs for data reduction and structure solution were taken from the X-RAY 72 system.[14] The Figures were prepared with the aid of the program ORTEP [15] and the co-ordination polyhedra analysed with the program POLY.[16]

The Patterson function calculated for the cerium compound was interpreted to yield two independent cerium atoms both lying on special positions (symmetry 222). The rest of the structure was solved by Fourier methods, the arsenic atom lying on a two-fold axis.

The thulium compound is almost isomorphous with the analogous compound $[PPh_4][Pr(S_2PMe_2)_4]$,[1] hence starting atomic co-ordinates were taken from this structure and successfully refined.

Final positional co-ordinates for all non-hydrogen atoms

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† *Supplementary data available* (No. SUP 23325; 22 pp.): observed and calculated structure factors, anisotropic (Ln, P, S, As), isotropic (C) thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Crystallographic data for $[AsPh_4][Ln(S_2PMe_2)_4]$

Ln	Ce	Tm
M	1 024.1	1 052.9
Crystal size/mm	0.27 × 0.19 × 0.17	0.38 × 0.12 × 0.09
Crystal system	tetragonal	orthorhombic
a/Å	11.461(2)	19.899(3)
b/Å		11.451(2)
c/Å	33.479(6)	19.051(2)
U/Å^3	4 398(1)	4 341(1)
Space group	$P4_222$	$Pca2_1$
D_m/g cm^{-3}	1.55	1.61
D_c/g cm^{-3}	1.56	1.61
F(000)	2 092	2 104
μ/cm^{-1}	30.3	34.5
Unique reflections	1 275	2 161
Reflections $I < 3\sigma$	504	698
No. of observations/ no of variables *	12.1	7.2
Structure solution	Patterson and Fourier	Refinement only
R	0.060	0.037
R'	0.072	0.031
Goodness of fit	5.54	2.41

In each case: $Z = 4$, Mo-K_α (niobium-filtered) radiation, λ 0.710 69 Å; 2θ—θ scan method, backgrounds scan-profile interpretation;[11] maximum $(\sin\theta)/\lambda$ 0.54; data collected $+h + k + l$. Refinement by full-matrix least squares; function minimised $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2$.

* Only those 'less-than's' (reflections with $I < 3\sigma$) with $|F_c| > |F_o|$ were included in the refinement.

Table 2. Atomic co-ordinates for $[AsPh_4][Ce(S_2PMe_2)_4]$

Atom	x	y	z
As	0	0.5	0.122 79(9)
Ce(1)	0	0	0
Ce(2)	0.5	0.5	0.25
P(1)	0.227 2(6)	0.101 9(6)	0.063 6(2)
P(2)	0.260 1(6)	0.580 2(7)	0.312 0(2)
S(1)	0.102 1(6)	0.205 0(6)	0.043 6(2)
S(2)	0.193 6(7)	−0.067 6(6)	0.055 8(2)
S(3)	0.404 0(7)	0.675 8(7)	0.304 9(2)
S(4)	0.280 9(7)	0.418 0(7)	0.291 2(2)
C(1)	0.369(3)	0.140(3)	0.040 3(8)
C(2)	0.251(2)	0.129(2)	0.117 3(6)
C(3)	0.138(2)	0.647(2)	0.288 2(7)
C(4)	0.215(2)	0.580(2)	0.364 5(7)
C(5)	0.138(2)	0.517(2)	0.091 0(6)
C(6)	0.132(2)	0.580(2)	0.054 1(8)
C(7)	0.244(2)	0.605(2)	0.036 0(6)
C(8)	0.345(2)	0.554(2)	0.049 5(7)
C(9)	0.343(2)	0.485(2)	0.084 2(7)
C(10)	0.237(2)	0.463(2)	0.103 1(6)
C(11)	0.008(2)	0.366(2)	0.155 4(6)
C(12)	0.077(2)	0.371(2)	0.189 2(7)
C(13)	0.082(2)	0.273(2)	0.215 1(7)
C(14)	0.023(2)	0.170(2)	0.203 1(6)
C(15)	−0.040(2)	0.165(2)	0.167 8(7)
C(16)	−0.050(2)	0.265(2)	0.140 8(6)

are reported in Tables 2 (Ce) and 3 (Tm). Derived bond lengths and angles for the two compounds are presented in Tables 4 (Ce) and 5 (Tm). Two views of $[Ln(S_2PMe_2)_4]^-$ are shown in Figures 1 and 2.

Table 3. Atomic co-ordinates for $[AsPh_4][Tm(S_2PMe_2)_4]$

Atom	x	y	z
As	0.528 9(1)	0.249 8(3)	0.378 3(1)
P(1)	0.250 6(3)	0.480 5(6)	0.143 7(3)
P(2)	0.030 7(3)	0.335 4(6)	0.206 9(3)
P(3)	0.195 3(3)	0.186 4(6)	0.425 4(3)
P(4)	0.300 6(3)	0.020 2(6)	0.222 6(3)
S(1)	0.277 7(3)	0.468 7(5)	0.243 4(4)
S(2)	0.206 7(3)	0.336 6(6)	0.110 6(3)
S(3)	0.094 1(2)	0.428 4(5)	0.264 5(3)
S(4)	0.065 0(3)	0.175 4(6)	0.194 4(4)
S(5)	0.150 6(3)	0.093 1(6)	0.349 4(3)
S(6)	0.216 3(3)	0.344 4(7)	0.389 4(4)
S(7)	0.322 0(2)	0.168 5(5)	0.272 2(3)
S(8)	0.217 3(3)	0.035 4(6)	0.168 4(3)
Tm	0.192 97(4)	0.256 4(1)	0.25
C(1)	0.194(1)	0.608(2)	0.134(1)
C(2)	0.321 7(8)	0.517(2)	0.084 2(9)
C(3)	−0.053 0(8)	0.339(2)	0.248(1)
C(4)	0.014(1)	0.404(2)	0.119(1)
C(5)	0.143(1)	0.192(2)	0.503(1)
C(6)	0.267 3(8)	0.115(2)	0.459 0(9)
C(7)	0.293 1(9)	−0.100(2)	0.284(1)
C(8)	0.372 7(9)	−0.025(2)	0.167(1)
C(9)	0.484 3(8)	0.117(2)	0.418(1)
C(10)	0.459 3(9)	0.128(2)	0.486(1)
C(11)	0.422 6(9)	0.030(2)	0.517(1)
C(12)	0.419(1)	−0.077(2)	0.480(1)
C(13)	0.449 1(9)	−0.085(2)	0.411(1)
C(14)	0.481 0(9)	0.011(2)	0.380(1)
C(15)	0.525 3(8)	0.242(2)	0.277 5(8)
C(16)	0.575 4(8)	0.174(2)	0.244(1)
C(17)	0.566 7(9)	0.165(2)	0.170(1)
C(18)	0.514(1)	0.227(2)	0.133(1)
C(19)	0.466 9(8)	0.287(2)	0.170 8(9)
C(20)	0.471 5(8)	0.298(1)	0.244(1)
C(21)	0.619 1(7)	0.254(2)	0.409 1(8)
C(22)	0.668 1(9)	0.324(2)	0.370(1)
C(23)	0.733 4(9)	0.320(2)	0.393(1)
C(24)	0.751 1(9)	0.255(2)	0.454(1)
C(25)	0.705(1)	0.190(2)	0.494(1)
C(26)	0.636 5(9)	0.185(2)	0.470(1)
C(27)	0.483 8(9)	0.387(2)	0.409 8(9)
C(28)	0.413 1(9)	0.384(2)	0.413(1)
C(29)	0.379 9(9)	0.484(2)	0.439(1)
C(30)	0.418(1)	0.578(2)	0.460(1)
C(31)	0.492(1)	0.583(2)	0.455(1)
C(32)	0.523 5(8)	0.483(2)	0.427(1)

Discussion

The lanthanide ion in both of these structures is surrounded by eight sulphur atoms. The average Ln–S distances are 2.991 (Ce) and 2.870 Å (Tm) in agreement with the lanthanide contraction. These may be compared with values of 2.976 Å in $[Pr(S_2PMe_2)_4]^-$,[1] 2.989 Å in $[La\{S_2P(OEt)_2\}_4]^-$,[9] 2.858 Å in $[Er\{S_2P(OEt)_2\}_4]^-$,[9] and 2.904 Å in $[Th(S_2PMe_2)_4]$[8] which are similarly eight-co-ordinate species, and values of 2.788, 2.741, and 2.692 Å found in the six-co-ordinate species $[Ln\{S_2P(C_6H_{11})_2\}_3]$ (Ln = Sm, Dy, or Lu respectively).[3,7]

Previously we have observed that the four-membered chelate rings tend to be close to planar.[9] In the present case they are significantly distorted from planarity, the deviation measured as the fold about the S···S direction varying from 15.0 to 18.5°. The angles at sulphur (Tables 4 and 5) are all close to 90°. Changes in the Ln–S bond lengths are accompanied by changes in the chelate angles at the metal ion and at phosphorus rather than at sulphur as we have shown previously.[9]

Table 4. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[AsPh_4][Ce(S_2PMe_2)_4]$ *

(*a*) Distances

Ce(1)-S(1)	3.005(8)A	Ce(2)-S(3)	2.939(8)B
Ce(1)-S(2)	3.004(8)B	Ce(2)-S(4)	3.014(8)A
P(1)-S(1)	1.97(1)	P(2)-S(3)	1.99(1)
P(1)-S(2)	2.00(1)	P(2)-S(4)	2.00(1)
P(1)-C(1)	1.85(3)	P(2)-C(3)	1.79(3)
P(1)-C(2)	1.84(2)	P(2)-C(4)	1.83(2)
As-C(5)	1.91(2)	As-C(11)	1.89(2)
S(1) ··· S(2)	3.32(1)	S(3) ··· S(4)	3.31(1)

(*b*) Angles

S(1)-Ce(1)-S(2)	67.1(2)	S(4)-Ce(2)-S(3)	67.4(2)
S(1)-Ce(1)-S(1′)	121.8(2)	S(4)-Ce(2)-S(4′)	125.6(2)
S(1)-Ce(1)-S(2′)	77.5(2)	S(4)-Ce(2)-S(3′)	79.2(2)
S(1)-Ce(1)-S(1″)	77.1(2)	S(4)-Ce(2)-S(4″)	71.9(2)
S(1)-Ce(1)-S(2″)	142.4(2)	S(4)-Ce(2)-S(3″)	137.7(2)
S(1)-Ce(1)-S(1‴)	134.2(2)	S(4)-Ce(2)-S(4‴)	136.7(2)
S(1)-Ce(1)-S(2‴)	79.2(2)	S(4)-Ce(2)-S(3‴)	80.3(2)
S(2)-Ce(1)-S(2′)	103.0(2)	S(3)-Ce(2)-S(3′)	102.7(2)
S(2)-Ce(1)-S(2″)	150.1(2)	S(3)-Ce(2)-S(3″)	154.6(2)
S(2)-Ce(1)-S(2‴)	84.7(2)	S(3)-Ce(2)-S(3‴)	83.0(2)
Ce(1)-S(1)-P(1)	88.8(3)	Ce(2)-S(3)-P(2)	90.5(3)
Ce(1)-S(2)-P(1)	88.4(3)	Ce(2)-S(4)-P(2)	88.3(3)
S(1)-P(1)-S(2)	113.5(5)	S(3)-P(2)-S(4)	111.7(5)
S(1)-P(1)-C(1)	110.6(9)	S(3)-P(2)-C(3)	111.0(9)
S(1)-P(1)-C(2)	109.6(8)	S(3)-P(2)-C(4)	110.6(9)
S(2)-P(1)-C(1)	110.2(9)	S(4)-P(2)-C(3)	109.9(9)
S(2)-P(1)-C(2)	108.5(7)	S(4)-P(2)-C(4)	111.5(9)
C(1)-P(1)-C(2)	104(1)	C(3)-P(2)-C(4)	102(1)
C(5)-As-C(11)	112(1)	C(5)-As-C(11′)	106(1)
C(5)-As-C(5′)	112.4(8)	C(11)-As-C(11′)	109.5(9)

Ph groups: C-C, 1.36(3)—1.47(3) Å; C-C-C, 113(2)—126(2)°.

* A and B refer to the two types of co-ordination site. Primed atoms are generated by symmetry.

The co-ordination polyhedra have been carefully analysed to permit comparisons with other structures of this type and with the n.m.r. studies. The analysis was performed by the method proposed by Dollase [17] using the computer program POLY.[16] The best description of the polyhedra was found to be the D_{2d} dodecahedron (*mmmm* isomer) in both cases; however, distortion towards the D_2 square antiprism is important. The calculated root-mean-square (r.m.s.) deviations from the dodecahedron are 0.074 [Ce(1)], 0.076 [Ce(2)], and 0.069 (Tm). The analogous deviations from the corresponding square antiprism are 0.097 [Ce(1)], 0.120 [Ce(2)], and 0.119 (Tm). A similar result was obtained for the complex $[PPh_4][Pr(S_2PMe_2)_4]$, the r.m.s. deviations being 0.084 and 0.116 from the dodecahedron and square antiprisms respectively.[1,16] In Figure 1 the complex is represented as a dodecahedron, and in Figure 2 as the corresponding square antiprism.

These results are in accord with the ligand–ligand repulsion energies for $M(bidentate)_4$ complexes calculated by Blight and Kepert.[18] These authors found the geometry of minimum energy to be a function of the ligand bite, *b*, defined as the intraligand sulphur–sulphur distance divided by the average metal–sulphur bond length. For $b < 1.00$ the most stable geometry is the D_{2d} dodecahedron, and for $1.00 < b < 1.15$ a smooth change to the D_2 square antiprism is expected. The observed values of *b* in the present study are 1.11 (Ce) and 1.13 (Tm) and would thus be expected to have the observed intermediate structures on the above grounds. However, this is not in accord with the observation that the complexes $[Ln\{S_2P(OEt_2\}_4]^-$ (Ln = La or Er) [9] and $[Th(S_2PMe_2)_4]$ [8] with b = 1.10, 1.14, and 1.14 respectively are almost perfectly dodecahedral. It has previously been noted by Drew [16] that the square antiprism is, in fact, rarely encountered for this type of complex.

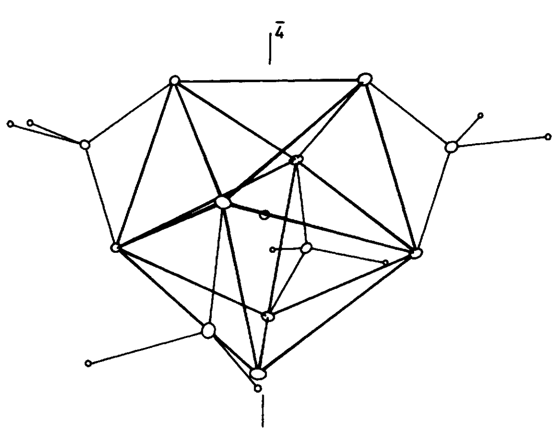

Figure 1. Compound $[Ln(S_2PMe_2)_4]^-$ viewed as a dodecahedron. The four-fold inversion axis of the ideal polyhedron is in the plane of the paper as marked

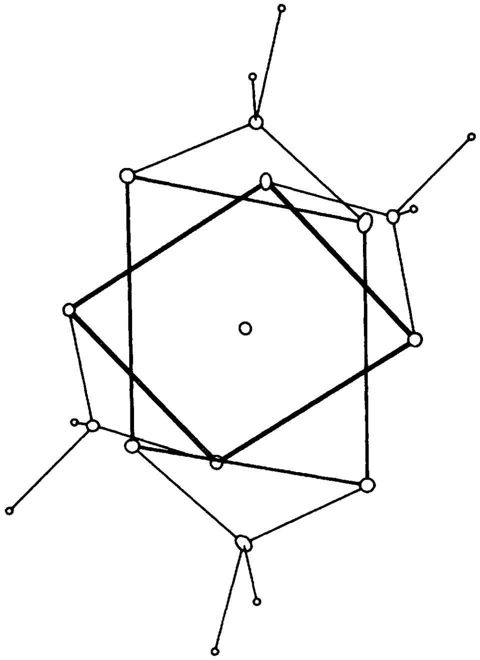

Figure 2. Compound $[Ln(S_2PMe_2)_4]^-$ viewed as a square antiprism. The eight-fold inversion axis of the ideal polyhedron is perpendicular to the plane of the paper

The individual values of the metal–sulphur bond lengths are worthy of comment. A dodecahedron has two different co-ordination sites, A and B, and $M-L_A$ is frequently observed to be longer than $M-L_B$.[16] In the case of the cerium compound this is clearly the case around Ce(2) where the A sites are occupied by S(4) and the B sites by S(3). In the case of Ce(1) there is no detectable difference between the two sites. However, it is Ce(1) which is the most distorted towards the square antiprism where both sites are equivalent. The thulium compound is quite typical, all the $M-L_A$ distances being longer than the corresponding $M-L_B$ ones. The A sites are occupied by S(1), S(4), S(6), and S(8) and the B sites by S(2), S(3), S(5),

Table 5. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[AsPh_4][Tm(S_2PMe_2)_4]$ *

(*a*) Distances

Tm–S(1)	2.961(6)A	Tm–S(5)	2.792(6)B	P(2)–S(3)	1.983(8)	P(4)–S(7)	1.989(9)
Tm–S(2)	2.824(6)B	Tm–S(6)	2.878(7)A	P(2)–S(4)	1.970(9)	P(4)–S(8)	1.962(8)
Tm–S(3)	2.798(5)B	Tm–S(7)	2.789(5)B	P(2)–C(3)	1.84(2)	P(4)–C(7)	1.81(2)
Tm–S(4)	2.909(6)A	Tm–S(8)	3.009(7)A	P(2)–C(4)	1.87(2)	P(4)–C(8)	1.86(2)
P(1)–S(1)	1.979(10)	P(3)–S(5)	2.008(8)	As–C(9)	1.92(2)	As–C(21)	1.89(1)
P(1)–S(2)	1.968(9)	P(3)–S(6)	1.979(9)	As–C(15)	1.92(2)	As–C(27)	1.91(2)
P(1)–C(1)	1.85(2)	P(3)–C(5)	1.81(2)	S(1) ··· S(2)	3.269(9)	S(5) ··· S(6)	3.252(9)
P(1)–C(2)	1.86(2)	P(3)–C(6)	1.77(2)	S(3) ··· S(4)	3.242(9)	S(7) ··· S(8)	3.252(8)

(*b*) Angles

S(1)–Tm–S(2)	68.8(2)	Tm–S(6)–P(3)	88.0(3)	S(3)–Tm–S(8)	139.1(2)	S(5)–P(3)–C(6)	111.8(7)
S(1)–Tm–S(3)	80.0(2)	Tm–S(7)–P(4)	92.3(2)	S(4)–Tm–S(5)	76.6(2)	S(6)–P(3)–C(5)	111.7(8)
S(1)–Tm–S(4)	138.1(2)	Tm–S(8)–P(4)	86.5(3)	S(4)–Tm–S(6)	126.0(2)	S(6)–P(3)–C(6)	112.3(7)
S(1)–Tm–S(5)	138.7(2)	S(1)–P(1)–S(2)	111.8(4)	S(4)–Tm–S(7)	138.2(2)	C(5)–P(3)–C(6)	100.8(9)
S(1)–Tm–S(6)	70.1(2)	S(1)–P(1)–C(1)	108.5(8)	S(4)–Tm–S(8)	71.6(2)	S(7)–P(4)–S(8)	110.8(4)
S(1)–Tm–S(7)	77.2(2)	S(1)–P(1)–C(2)	113.2(6)	S(5)–Tm–S(6)	70.0(2)	S(7)–P(4)–C(7)	111.3(7)
S(1)–Tm–S(8)	125.2(2)	S(2)–P(1)–C(1)	111.1(8)	S(5)–Tm–S(7)	86.2(2)	S(7)–P(4)–C(8)	110.0(7)
S(2)–Tm–S(3)	86.1(2)	S(2)–P(1)–C(2)	109.3(7)	S(5)–Tm–S(8)	80.5(2)	S(8)–P(4)–C(7)	109.6(7)
S(2)–Tm–S(4)	81.1(2)	C(1)–P(1)–C(2)	102.6(9)	S(6)–Tm–S(7)	80.7(2)	S(8)–P(4)–C(8)	112.1(7)
S(2)–Tm–S(5)	152.3(2)	S(3)–P(2)–S(4)	110.2(4)	S(6)–Tm–S(8)	138.2(2)	C(7)–P(4)–C(8)	102.8(9)
S(2)–Tm–S(6)	137.6(2)	S(3)–P(2)–C(3)	109.1(8)	S(7)–Tm–S(8)	68.0(2)	C(9)–As–C(15)	109.6(9)
S(2)–Tm–S(7)	99.9(2)	S(3)–P(2)–C(4)	112.4(7)	Tm–S(1)–P(1)	86.6(3)	C(9)–As–C(21)	109.7(9)
S(2)–Tm–S(8)	176.8(2)	S(4)–P(2)–C(3)	112.9(7)	Tm–S(2)–P(1)	90.8(3)	C(9)–As–C(27)	108.3(8)
S(3)–Tm–S(4)	69.2(2)	S(4)–P(2)–C(4)	110.1(7)	Tm–S(3)–P(2)	90.9(3)	C(15)–As–C(21)	110.3(7)
S(3)–Tm–S(5)	101.1(2)	C(3)–P(2)–C(4)	102(1)	Tm–S(4)–P(2)	87.9(3)	C(15)–As–C(27)	109.6(9)
S(3)–Tm–S(6)	77.0(2)	S(5)–P(3)–S(6)	109.3(4)	Tm–S(5)–P(3)	89.9(3)	C(21)–As–C(27)	109.2(9)
S(3)–Tm–S(7)	152.4(2)	S(5)–P(3)–C(5)	110.8(7)				

Ph groups: C–C, 1.37(3)—1.48(3) Å; C–C–C, 113(2)—126(2)°.

* A and B refer to the two types of co-ordination site.

Table 6. Angles (θ/°) between the Ln–P vector and the principal symmetry axis for $[Ln(S_2PR_2)_4]^{n-}$, and values of $(3\cos^2\theta - 1)$

Compound			Dodecahedron		Square antiprism		
Ln	R	*n*	θ	$(3\cos^2\theta - 1)$	θ	$(3\cos^2\theta - 1)$	Ref.
Ce	Me	1	69.8	−0.64	53.8	0.05	This work
Tm	Me	1	68.8	−0.61	53.6	0.06	This work
Pr	Me	1	68.9	−0.61	54.0	0.04	1
La	OEt	1	66.8	−0.53	51.5	0.16	9
Er	OEt	1	67.6	−0.56	51.5	0.16	9
Th	Me	0	68.4	−0.59	52.5	0.11	8
Th	C_6H_{11}	0	66.2	−0.51	50.3	0.22	8
$M(L\text{–}L)_4$		min.	66.1	−0.51	54.7	0.00	16
		max.	73.1	−0.75	57.4	−0.013	

and S(7). The values are given in Tables 4 and 5 with the type of site reported after the distance.

In the following paper [10] it is shown that there is an abrupt change in the solution structure for this series of complexes which occurs at dysprosium. This conclusion is based on the observation of a sudden change in the hyperfine coupling and in the relative dipolar shift of the phosphorus nuclei obtained from the n.m.r. spectra in CD_2Cl_2 solution. The ^{31}P hyperfine coupling constant for the light ions is *ca.* 2 times that for the heavy ones. The ^{31}P dipolar shift relative to the methyl protons is 32.0 for the light ions and −2.4 (almost zero) for the heavy ones. This observation is allowed by the fact that the average proton positions observed for these fluxional molecules are fortuitously similar for both the heavy and light ions. This can be seen by plotting their isotropic shifts against the so-called Bleaney factors (see Figure 2 in the following paper). This also indicates that the magnetic properties for the light and heavy ions must behave similarly, hence the only origin for the observations made on the ^{31}P resonance must be geometrical.

We have previously shown that a similar change in solution structure occurs in the series $[Ln\{S_2P(OEt)_2\}_4]^-$ at Ln = Ho.[5] However, the corresponding solid state structures for lanthanum and erbium were shown to be isostructural,[9] and the co-ordination polyhedra to be almost perfect D_{2d} dodecahedra rather than the intermediate geometry observed in the present case. The change in solution structure was demonstrated to be from dodecahedral for the light ions to square-antiprismatic for the heavy ones. We may employ the same argument in the present case and show that a similar conclusion may be reached.

The dipolar shift Δ in the axial approximation (which is valid for the present series of compounds) may be written as a function of the complex geometry [equation (i)], where *r* is the

$$\Delta \propto (3\cos^2\theta - 1)r^{-3} \qquad \text{(i)}$$

radius vector from the paramagnetic ion to the observed 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,[9] 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 change in the angle θ.

In Table 6 we present the angle θ observed between the vector *r* and the four-fold inversion axis for a number of structures of the present type and the related value of $(3\cos^2\theta - 1)$. On the basis of these predominantly dodecahedral structures we may calculate the value of θ that would be obtained between *r* and the pseudo-eight-fold inversion axis if they were transformed into the corresponding square antiprism by the mechanism described above. These values are also reported in Table 6 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.[16] In this calculation we have made the assumption that the chelates are all planar. From Table 6 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 n.m.r. results strongly suggest that these are the two most likely structures in solution. This does not mean that they exist as stable entities, but that they occupy a potential minimum on the fluxional reaction co-ordinate. For the light ions, the minimum is the dodecahedron and the square antiprism represents the transition state on the rearrangement co-ordinate, and for the heavy ions the converse is true. The present structures have frozen out a part of the reaction co-ordinate whereas previous structures in this series showed only the dodecahedral starting point.[8,9]

It is, of course, tempting to ascribe the difference in behaviour between the solid and solution to packing forces in the crystal. However, when only minor differences are found in the molecular structures in totally different crystal environments as in the present case, this reasoning must be abandoned. Indeed, the difference between the two independent polyhedra found in the cerium compound is of the same order as that between these polyhedra and the thulium or praseodymium [1] analogues. Thus the factors determining the structures in the solid or in solution remain obscure.

Similar structural and n.m.r. results have been obtained for analogous systems where the substituents are OMe, OPr^i, and Et. These results will be reported in the near future.[19]

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