Crystal and Molecular Structures of $[AsPh_4][Ln\{S_2P(OEt)_2\}_4]$ (Ln = La or Er) and Their Comparison with Results obtained in Solution from Paramagnetic Nuclear Magnetic Resonance Data

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The crystal structures of the title compounds have been determined from diffractometer data. The crystals of both compounds are monoclinic, space group $P2_1/c$, and have four molecules in unit cells of dimensions: Ln = La, a = 20.053(7), b = 15.207(3), c = 20.389(4) Å, β = 112.02(2)° (R = 0.071); Ln = Er, a = 19.972(3), b = 15.148(2), c = 20.244(3) Å, β = 112.27(1)° (R = 0.059). In both cases the lanthanide ion is co-ordinated to eight sulphur atoms, the average Ln–S distances being 2.989 (La) and 2.858 Å (Er). The co-ordination polyhedra are both almost perfect D_{2d} dodecahedra (*mmmm* isomer). Although the compounds have similar structures in the solid state, in solution they are quite different as demonstrated by paramagnetic n.m.r. data. The change in the observed ^{31}P dipolar shift is shown to be in accord with a change from dodecahedral to square antiprismatic geometry for such compounds when Ln = holmium.

WE have been investigating dithiophosphinate (S_2PR_2) complexes of the lanthanides (Ln) for several years,[1] and it is now clear that the co-ordination of sulphur donors to the lanthanides is no longer to be considered unusual. To date, the only structure reported for a $[Ln(S_2PR_2)_4]^-$ species is $[Pr(S_2PMe_2)_4]^-$ as its PPh_4^+ salt;[2] hence we were moved to determine some more structures of this type, especially after the observation that the structure of $[Th(S_2PMe_2)_4]$ is quite different from that of the praseodymium analogue.[3] The praseodymium compound has a co-ordination polyhedron intermediate between a dodecahedron and a square antiprism, whereas the thorium complex is perfectly dodecahedral. An additional motivation for this study was the current interest in the study of the reaction co-ordinate for rearrangement between different polyhedra frozen in the solid state,[4] especially for high co-ordination numbers.

We have already extensively studied the compounds $[Ln(S_2PR_2)_4]^-$ where R = OEt and found an anomaly in our results.[5,6] X-Ray powder-diffraction patterns of the $AsPh_4^+$ salts indicated no change in the solid-state structure along the series La—Lu. However, this is clearly not the case in solution. N.m.r. measurements show that there must be a clean structural break at Ho, based on the observation of an abrupt reduction in the ^{31}P hyperfine coupling constant by a factor of 1.8 and in the relative dipolar shift by a factor of 13.6.

We have thus carried out structure determinations on the two title compounds, one ante-holmium and one post-holmium, in the hope that the direction of any observed distortion of the co-ordination polyhedron due to changes in the ionic radii would allow us to interpret the changes observed in solution.

It is to be noted that further n.m.r. experiments have indicated similar structural changes with other substituents at phosphorus, and this work will be reported in due course.[7]

EXPERIMENTAL

The complexes $[AsPh_4][Ln\{S_2P(OEt)_2\}_4]$ (Ln = La or Er) were prepared by the literature method.[5] Suitable crystals for X-ray studies were obtained by recrystallisation from ethanol (La) or ethanol–isopropyl alcohol (Er). The lanthanum compound is stable in air and required no special precautions. The erbium analogue is, however, easily hydrolysed and was handled under dry argon. The crystal used for X-ray measurements (Er) was thus mounted 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, and corrected for absorption as previously reported.[1] The crystal data, measurement methods (backgrounds by scan-profile interpretation [8]), structure solution, and refinement are summarised in Table 1. Scattering factors for the neutral atoms were taken from Cromer and Mann,[9] and anomalous-scattering coefficients from Cromer and Liberman.[10] Computer programs for data reduction and structure

TABLE 1

Crystallographic data for $[AsPh_4][Ln\{S_2P(OEt)_2\}_4]$

Ln	La	Er
M	1 263.2	1 291.5
Crystal size/mm	0.11 × 0.16 × 0.21	0.25 × 0.35 × 0.36
a/Å	20.053(7)	19.972(3)
b/Å	15.207(3)	15.148(2)
c/Å	20.389(4)	20.244(3)
β/°	112.02(2)	112.27(1)
U/Å^3	5 764(2)	5 668(1)
D_m/g cm^{-3}	1.46	1.53
D_c/g cm^{-3}	1.46	1.52
F(000)	2 568	2 612
μ/cm^{-1}	17.9	25.61
Unique reflections	5 823	5 704
Reflections $<3\sigma$	3 786	1 864
No. of observations/ no. of variables *	12.1	15.2
Structure solution	Refinement only	MULTAN and Fourier
R	0.071	0.059
R'	0.061	0.068
Goodness of fit	1.54	2.87

In each case: crystal system, monoclinic; space group $P2_1/c$; $Z = 4$; Mo-K_α (niobium-filtered) radiation, λ 0.710 69 Å; 2θ–θ scan method; maximum (sinθ)/λ 0.50; data collected, $+h + k \pm l$. Refinement by block-diagonal least squares; function minimised, $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2$.

* All $I > 3\sigma(I)$ reflections and those $I < 3\sigma(I)$ reflections for which $|F_c| > |F_o|$ were included in the refinement.

solution were taken from the '*X*-Ray '72' system.[11] Initial phases were generated with the program MULTAN,[12] the Figure was prepared with the program ORTEP,[13] and the co-ordination polyhedra were analysed with the program POLY.[4]

Initially, the structure of the erbium compound was solved using direct and Fourier methods. The resulting atomic co-ordinates were used as the starting point for the refinement of the lanthanum structure. Final positional co-ordinates for all non-hydrogen atoms are listed in Tables 2 (La) and 3 (Er). Derived bond lengths and angles for the two compounds are summarised in Table 4. A perspective drawing of one complex is shown in the Figure. The ethoxy-groups have been omitted for clarity. Final observed and calculated structure factors as well as tables of anisotropic (Ln, P, S, As) and isotropic (O, C) thermal parameters are available in Supplementary Publication No. SUP 23049 (47 pp.).*

TABLE 2

Atomic co-ordinates for $[AsPh_4][La\{S_2P(OEt)_2\}_4]$

Atom	*X*	*Y*	*Z*
La	0.751 75(7)	0.857 90(8)	0.954 08(5)
P(1)	0.560 4(3)	0.862 3(4)	0.873 4(3)
P(2)	0.785 9(3)	0.645 3(5)	1.033 4(3)
P(3)	0.880 2(3)	0.975 4(4)	1.099 6(3)
P(4)	0.772 6(4)	0.952 9(4)	0.801 2(3)
S(1)	0.619 9(3)	0.778 5(4)	0.845 1(3)
S(2)	0.613 7(3)	0.931 4(4)	0.957 8(3)
S(3)	0.735 1(3)	0.738 8(4)	1.062 6(3)
S(4)	0.811 0(3)	0.677 2(3)	0.951 6(3)
S(5)	0.904 7(3)	0.880 1(4)	1.046 9(3)
S(6)	0.776 5(3)	0.999 0(4)	1.061 7(3)
S(7)	0.811 2(3)	0.835 7(4)	0.840 1(3)
S(8)	0.735 7(3)	1.018 0(4)	0.864 4(3)
As	0.752 0(1)	0.145 7(2)	0.300 8(1)
O(1)	0.515 2(7)	0.923 2(9)	0.807 5(7)
O(2)	0.493 1(8)	0.813 9(9)	0.880 4(8)
O(3)	0.857 4(8)	0.614 1(9)	1.095 8(8)
O(4)	0.741 4(8)	0.555 8(9)	1.019 6(6)
O(5)	0.908 1(7)	0.960 2(9)	1.181 3(7)
O(6)	0.927 7(6)	1.060 7(7)	1.102 6(5)
O(7)	0.830 4(8)	1.009 3(9)	0.782 5(7)
O(8)	0.714 8(8)	0.946 6(9)	0.722 4(7)
C(1)	0.533(1)	1.006(2)	0.795(1)
C(2)	0.484(1)	1.043(1)	0.728(1)
C(3)	0.503(2)	0.752(2)	0.944(2)
C(4)	0.451(2)	0.710(3)	0.936(2)
C(5)	0.864(1)	0.604(1)	1.170(1)
C(6)	0.947(1)	0.618(2)	1.209(1)
C(7)	0.667(1)	0.553(1)	0.965(1)
C(8)	0.635(1)	0.462(1)	0.971(1)
C(9)	0.882(1)	0.887(1)	1.208(1)
C(10)	0.921(1)	0.883(1)	1.289(1)
C(11)	0.933(1)	1.098(2)	1.039(1)
C(12)	0.973(1)	1.179(1)	1.060(1)
C(13)	0.891(1)	1.050(2)	0.842(1)
C(14)	0.917(1)	1.119(2)	0.806(1)
C(15)	0.666(1)	0.879(2)	0.697(1)
C(16)	0.606(1)	0.904(1)	0.633(1)
C(17)	0.714(1)	0.037(1)	0.255 3(9)
C(18)	0.732(1)	−0.044(1)	0.291 3(9)
C(19)	0.704(1)	−0.121(1)	0.254(1)
C(20)	0.658 4(9)	−0.117(1)	0.184 8(8)
C(21)	0.634(1)	−0.037(1)	0.149(1)
C(22)	0.664(1)	0.045(1)	0.184(1)
C(23)	0.691(1)	0.202(1)	0.339 4(9)
C(24)	0.719(1)	0.256(1)	0.402(1)
C(25)	0.673(1)	0.295(1)	0.430(1)
C(26)	0.597(1)	0.289(1)	0.390(1)
C(27)	0.569(1)	0.231(1)	0.329(1)
C(28)	0.615(1)	0.188(1)	0.302 4(9)
C(29)	0.762(1)	0.217(1)	0.229 2(9)
C(30)	0.733(1)	0.307(1)	0.220 9(9)
C(31)	0.742(1)	0.360(1)	0.164(1)
C(32)	0.777(1)	0.320(1)	0.121(1)
C(33)	0.806(1)	0.234(2)	0.130(1)
C(34)	0.799(1)	0.182(1)	0.185(1)
C(35)	0.842(1)	0.126(1)	0.378 1(8)
C(36)	0.840(1)	0.086(1)	0.440(1)
C(37)	0.908(1)	0.073(1)	0.496(1)
C(38)	0.969(1)	0.103(1)	0.491(1)
C(39)	0.974(1)	0.144(1)	0.429(1)
C(40)	0.904(1)	0.157(1)	0.369 5(9)

TABLE 3

Atomic co-ordinates for $[AsPh_4][Er\{S_2P(OEt)_2\}_4]$

Atom	*X*	*Y*	*Z*
Er	0.752 22(4)	0.856 83(4)	0.955 80(3)
P(1)	0.565 7(2)	0.861 0(3)	0.873 2(2)
P(2)	0.784 1(2)	0.650 7(3)	1.034 3(2)
P(3)	0.879 5(2)	0.967 3(3)	1.097 5(2)
P(4)	0.770 9(2)	0.950 9(3)	0.808 6(2)
S(1)	0.629 6(2)	0.778 6(3)	0.849 7(2)
S(2)	0.619 2(2)	0.929 4(3)	0.959 7(2)
S(3)	0.733 4(2)	0.748 3(3)	1.060 8(2)
S(4)	0.807 9(2)	0.680 3(2)	0.951 5(2)
S(5)	0.899 8(2)	0.874 5(3)	1.039 8(2)
S(6)	0.775 4(2)	0.991 6(3)	1.061 9(2)
S(7)	0.809 2(2)	0.833 2(2)	0.844 8(2)
S(8)	0.738 0(2)	1.012 9(2)	0.876 0(2)
As	0.750 30(8)	0.145 1(1)	0.300 95(7)
O(1)	0.520 7(5)	0.920 5(7)	0.806 8(5)
O(2)	0.496 5(6)	0.811 1(7)	0.877 5(5)
O(3)	0.856 8(6)	0.619 9(7)	1.095 9(6)
O(4)	0.740 1(5)	0.559 5(6)	1.022 6(5)
O(5)	0.912 6(5)	0.948 6(6)	1.181 1(5)
O(6)	0.927 0(5)	1.053 2(6)	1.103 6(5)
O(7)	0.826 2(5)	1.008 1(6)	0.787 0(5)
O(8)	0.709 0(6)	0.949 4(7)	0.731 7(6)
C(1)	0.536(1)	1.008(1)	0.793(1)
C(2)	0.483(1)	1.043(1)	0.725(1)
C(3)	0.509(1)	0.743(1)	0.937(1)
C(4)	0.450(2)	0.714(2)	0.939(2)
C(5)	0.865(1)	0.612(1)	1.172(1)
C(6)	0.947(1)	0.617(1)	1.214(1)
C(7)	0.667 2(9)	0.558(1)	0.967 9(8)
C(8)	0.635 8(9)	0.466(1)	0.971 4(9)
C(9)	0.880(1)	0.881(1)	1.208(1)
C(10)	0.921(1)	0.884(1)	1.291(1)
C(11)	0.927 3(9)	1.094(1)	1.037 2(9)
C(12)	0.970(1)	1.182(1)	1.060 6(9)
C(13)	0.894(1)	1.039(1)	0.845 2(9)
C(14)	0.914(1)	1.113(1)	0.815(1)
C(15)	0.674(1)	0.882(1)	0.692(1)
C(16)	0.604(1)	0.898(1)	0.634(1)
C(17)	0.709 1(7)	0.038 8(9)	0.255 1(7)
C(18)	0.732 8(8)	−0.043(1)	0.289 4(7)
C(19)	0.703 3(9)	−0.121(1)	0.249 8(8)
C(20)	0.655 3(8)	−0.118 4(9)	0.180 7(7)
C(21)	0.629 6(9)	−0.038(1)	0.147 7(8)
C(22)	0.659 1(8)	0.044(1)	0.184 0(8)
C(23)	0.687 8(7)	0.200 7(8)	0.340 1(7)
C(24)	0.716 8(8)	0.253 3(9)	0.401 2(7)
C(25)	0.669 5(9)	0.294(1)	0.427 4(8)
C(26)	0.595 5(9)	0.288(1)	0.392 0(8)
C(27)	0.565 4(9)	0.234(1)	0.330 4(9)
C(28)	0.614 9(8)	0.190 7(9)	0.304 5(7)
C(29)	0.761 5(8)	0.218 1(9)	0.228 8(7)
C(30)	0.733 9(7)	0.306 3(9)	0.221 2(7)
C(31)	0.743 9(8)	0.357(1)	0.165 3(8)
C(32)	0.776 7(9)	0.322(1)	0.122 3(9)
C(33)	0.803 4(9)	0.235(1)	0.131 3(9)
C(34)	0.797 2(8)	0.182(1)	0.187 1(8)
C(35)	0.841 4(7)	0.126 2(8)	0.379 4(7)
C(36)	0.839 5(8)	0.083(1)	0.439 6(8)
C(37)	0.907 7(9)	0.073(1)	0.499 7(8)
C(38)	0.972 5(9)	0.102(1)	0.493 5(8)
C(39)	0.974 7(9)	0.142(1)	0.432 4(8)
C(40)	0.904 1(8)	0.153 5(9)	0.371 5(7)

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 4

Bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[AsPh_4][Ln\{S_2P(OEt)_2\}_4]$

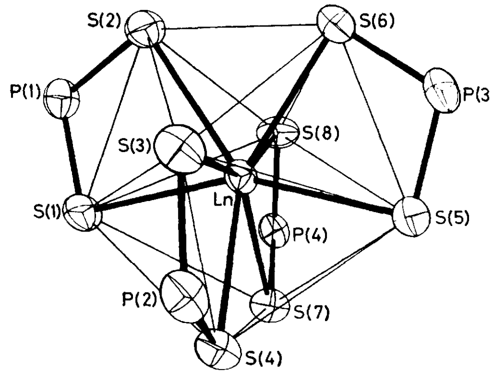
(a) Distances	La	Er
Ln–S(1)	2.997(5)	2.834(4)
Ln–S(2)	3.013(7)	2.904(5)
Ln–S(3)	2.973(6)	2.824(4)
Ln–S(4)	3.002(5)	2.910(4)
Ln–S(5)	2.959(5)	2.803(4)
Ln–S(6)	2.975(6)	2.871(4)
Ln–S(7)	3.003(7)	2.900(5)
Ln–S(8)	2.989(6)	2.817(4)
P(1)–S(1)	1.974(9)	1.969(6)
P(1)–S(2)	1.956(7)	1.965(5)
P(1)–O(1)	1.60(1)	1.58(1)
P(1)–O(2)	1.59(2)	1.60(1)
P(2)–S(3)	1.968(9)	1.978(6)
P(2)–S(4)	1.974(9)	1.960(6)
P(2)–O(3)	1.59(1)	1.58(1)
P(2)–O(4)	1.59(1)	1.61(1)
P(3)–S(5)	1.973(9)	1.966(6)
P(3)–S(6)	1.962(9)	1.961(6)
P(3)–O(5)	1.56(1)	1.59(1)
P(3)–O(6)	1.60(1)	1.59(1)
P(4)–S(7)	1.986(8)	1.968(5)
P(4)–S(8)	1.976(9)	1.965(7)
P(4)–O(7)	1.60(2)	1.59(1)
P(4)–O(8)	1.59(1)	1.59(1)
As–C(17)	1.91(2)	1.88(1)
As–C(23)	1.89(2)	1.91(2)
As–C(29)	1.89(2)	1.91(2)
As–C(35)	1.92(1)	1.93(1)
S(1) · · · S(2)	3.303(9)	3.251(6)
S(3) · · · S(4)	3.302(9)	3.268(7)
S(5) · · · S(6)	3.250(9)	3.219(7)
S(7) · · · S(8)	3.286(9)	3.242(6)

(b) Angles	La	Er
S(1)–Ln–S(2)	66.7(2)	69.0(1)
S(1)–Ln–S(3)	89.5(2)	92.1(1)
S(1)–Ln–S(4)	82.2(2)	79.8(1)
S(1)–Ln–S(5)	159.3(2)	155.3(1)
S(1)–Ln–S(6)	134.0(2)	135.4(1)
S(1)–Ln–S(7)	82.9(2)	80.9(1)
S(1)–Ln–S(8)	90.7(2)	92.6(1)
S(2)–Ln–S(3)	81.2(2)	79.4(1)
S(2)–Ln–S(4)	135.5(2)	135.4(1)
S(2)–Ln–S(5)	133.2(2)	135.3(1)
S(2)–Ln–S(6)	67.3(2)	66.5(1)
S(2)–Ln–S(7)	134.1(2)	134.4(1)
S(2)–Ln–S(8)	79.9(2)	78.7(1)
S(3)–Ln–S(4)	67.1(2)	69.5(1)
S(3)–Ln–S(5)	88.4(2)	90.5(1)
S(3)–Ln–S(6)	85.7(2)	83.1(1)
S(3)–Ln–S(7)	134.1(2)	135.7(1)
S(3)–Ln–S(8)	159.2(2)	155.2(1)
S(4)–Ln–S(5)	78.1(2)	77.3(1)
S(4)–Ln–S(6)	135.7(1)	136.1(1)
S(4)–Ln–S(7)	67.0(2)	66.2(1)
S(4)–Ln–S(8)	133.5(2)	135.3(1)
S(5)–Ln–S(6)	66.4(2)	69.1(1)
S(5)–Ln–S(7)	83.7(2)	81.4(1)
S(5)–Ln–S(8)	98.4(2)	97.0(1)
S(6)–Ln–S(7)	130.4(2)	131.9(1)
S(6)–Ln–S(8)	79.3(2)	77.6(1)
S(7)–Ln–S(8)	66.5(2)	69.1(1)
Ln–S(1)–P(1)	89.2(2)	90.3(2)
Ln–S(2)–P(1)	89.0(3)	88.3(2)
Ln–S(3)–P(2)	90.0(3)	90.1(2)
Ln–S(4)–P(2)	89.0(3)	88.0(2)
Ln–S(5)–P(3)	91.2(3)	91.3(2)
Ln–S(6)–P(3)	91.0(3)	89.4(2)
Ln–S(7)–P(4)	89.9(3)	88.1(2)
Ln–S(8)–P(4)	90.5(3)	90.5(2)
S(1)–P(1)–S(2)	114.4(4)	111.5(2)
S(1)–P(1)–O(1)	109.9(7)	111.5(5)
S(1)–P(1)–O(2)	110.7(7)	111.3(5)
S(2)–P(1)–O(1)	112.2(6)	113.5(4)
S(2)–P(1)–O(2)	111.9(6)	112.9(5)
O(1)–P(1)–O(2)	96.4(8)	95.2(6)
S(3)–P(2)–S(4)	113.8(4)	112.1(2)
S(3)–P(2)–O(3)	112.8(7)	114.7(5)
S(3)–P(2)–O(4)	110.5(7)	112.0(5)
S(4)–P(2)–O(3)	108.1(8)	107.1(6)
S(4)–P(2)–O(4)	111.4(6)	111.5(5)
O(3)–P(2)–O(4)	99.4(8)	98.6(5)
S(5)–P(3)–S(6)	111.4(3)	110.2(2)
S(5)–P(3)–O(5)	114.2(6)	114.2(4)
S(5)–P(3)–O(6)	110.5(7)	112.4(5)
S(6)–P(3)–O(5)	110.5(7)	112.3(5)
S(6)–P(3)–O(6)	113.3(6)	113.2(4)
O(5)–P(3)–O(6)	96.3(7)	93.9(5)
S(7)–P(4)–S(8)	112.1(4)	111.1(3)
S(7)–P(4)–O(7)	111.5(7)	112.6(4)
S(7)–P(4)–O(8)	112.1(6)	113.8(5)
S(8)–P(4)–O(7)	111.6(6)	112.3(4)
S(8)–P(4)–O(8)	112.2(7)	110.4(5)
O(7)–P(4)–O(8)	96.3(8)	95.9(6)
C(17)–As–C(23)	113.1(9)	110.4(6)
C(17)–As–C(29)	105.1(8)	105.9(6)
C(17)–As–C(35)	109.9(7)	112.2(5)
C(23)–As–C(29)	109.4(9)	110.3(4)
C(23)–As–C(35)	106.5(8)	106.5(6)
C(29)–As–C(35)	113.0(8)	111.6(6)

OEt groups: Ln = La, O–C 1.37(3)—1.55(4), C–C 1.18(6)—1.56(3) Å; P–O–C 118(1)—126(1), O–C–C 102(2)—113(2)°; Ln = Er, O–C 1.32(2)—1.53(3), C–C 1.28(4)—1.56(3) Å; P–O–C 118(1)—130(1), O–C–C 103(1)—119(2)°. The large range of values and high e.s.d.s of the OEt groups is associated with their high thermal motion. Ph groups: Ln = La, C–C 1.33(4)—1.48(3) Å, C–C–C 114(2)—126(2)°; Ln = Er, C–C 1.37(2)—1.49(2) Å, C–C–C 116(2)—124(1)°. S(2), S(4), S(6), and S(7) occupy A sites and S(1), S(3), S(5), and S(8) occupy B sites in the dodecahedron.

DISCUSSION

In both structures the lanthanide ion is surrounded by eight sulphur atoms. The average Ln–S bond lengths are 2.989 (La) and 2.858 Å (Er) in agreement with the lanthanide contraction. These may be compared with 2.976 Å in $[Pr(S_2PMe_2)_4]^-$,[2] 2.991 Å in $[Ce(S_2PMe_2)_4]^-$,[7] and 2.904 Å in $[Th(S_2PMe_2)_4]$ [3] which are all eight-co-ordinate, and 2.788, 2.741, and 2.692 Å for $[Ln\{S_2P(C_6H_{11})_2\}_3]$ (Ln = Sm, Dy, or Lu), which are six-co-ordinate.[1]



Co-ordination polyhedron of the $[Ln\{S_2P(OEt)_2\}_4]^-$ anion, the ethoxy-groups being omitted for clarity

The four-membered chelate rings are almost planar, the deviations measured as the fold angle about the S–S direction varying from 0.8 to 12.6°, and the angles at sulphur are all close to 90° (Table 4). As seen in previous structures,[1,2,3,7] changing the Ln–S bond length does not affect the angle at sulphur, but is accompanied by changes in the S–Ln–S and S–P–S angles.

The co-ordination polyhedra are almost perfect D_{2d} dodecahedra (*mmmm* isomers). The analysis of the polyhedra was carried out with the computer program POLY[4] which is based on the method proposed by Dollase.[14] The calculated root-mean-square (r.m.s.) deviations from the dodecahedron are 0.039 (La) and 0.029 Å (Er). A dodecahedron has two different co-ordination sites A and B, and it is often observed that $M–L_A$ is greater than $M–L_B$.[4] This is clearly the case for the erbium compound; however, although the same observation can be made for the lanthanum analogue, the differences are hardly significant. This phenomenon is not reflected in any asymmetry of the bonds in the PS_2 unit, no significant differences being observed.

TABLE 5

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	$(3\cos^2\theta - 1)$	*R* *
(1)	La	OEt	1	66.8	−0.53	51.5	0.16	−3.3
(2)	Er	OEt	1	67.6	−0.56	51.5	0.16	−3.5
(3)	Ce	Me	1	69.8	−0.64	53.8	0.05	−12.8
(4)	Pr	Me	1	68.9	−0.61	54.0	0.04	−15.3
(5)	Th	Me	0	68.4	−0.59	52.5	0.11	−5.4

* The ratio of the values of $(3\cos^2\theta - 1)$ for the dodecahedron and square antiprism.

Blight and Kepert[15] have calculated the ligand–ligand repulsion energies and hence the expected geometries for M(bidentate ligand)$_4$ systems as a function of the ligand bite. The bite, *b*, is defined as the average 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* for the present structures are 1.10 (La) and 1.14 (Er), thus the observation of almost perfect dodecahedra with no evidence for a distortion towards the square antiprism is at first sight a little surprising, especially in view of the n.m.r. results discussed below. However, these are far from the first structures found to be more dodecahedral than predicted, and this is in fact a quite common co-ordination polyhedron for M(bidentate ligand)$_4$ systems, even with bites as large as 1.14.[4]

In solution, it was reported that there was an abrupt change in the structure of these complexes at holmium.[6] The argument was based on a sudden change in the hyperfine coupling and, more important, in the relative dipolar shift of the phosphorus nuclei observed in the n.m.r. spectra of the complexes of the light and heavy ions. The ^{31}P dipolar shift for the light ions was found to be 13.6 times greater than that observed for the heavy ions. No such break was observed for the proton dipolar shifts, however. This suggests that the magnetic properties of the two different structures are similar, and that the average proton positions in these fluxional molecules are also similar.

In the axial approximation, we may write the dipolar shift as a function of geometrical terms as in equation (i) where *r* is the radius vector from the paramagnetic ion

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

to the observed nucleus and θ is the angle between the principal axis of the magnetic-susceptibility tensor and the vector *r*. Clearly *r* does not vary enough, despite the lanthanide contraction, to account for a sudden change of an order of magnitude in the phosphorus dipolar shift, hence we conclude that the parameter that changes must be θ.*

If we consider the principal axis of the magnetic-susceptibility tensor to be collinear with the main symmetry axis, we can look at the ideal possible structures. As we have seen above, the two ideal structures are the dodecahedron and the square antiprism. In the dodecahedron, the principal axis is the four-fold inversion axis. The values of the angle (θ) observed between this axis and the Ln–P vector for a number of compounds are given in Table 5 together with the corresponding value of $(3\cos^2\theta - 1)$, and the average values are 68.3° and −0.59. In the square antiprism, the principal axis is the eight-fold, or in our case pseudo-eight-fold, inversion axis. The observed values of the angle (θ) between this axis and the Ln–P vector are also given in Table 5 with the corresponding values of $(3\cos^2\theta - 1)$, and the average values are 52.7° and +0.10. It is to be emphasised that these are values taken from distorted structures or from predominantly dodecahedral structures and are thus not as precise as we would like, especially the values of θ for the square antiprism. However, it is clear that θ (dodecahedral) is larger than θ (square antiprism) and evaluation of $(3\cos^2\theta - 1)$ reveals a ratio of −3 : −15. It is clear, especially for the two structures (3) and (4) which are considerably distorted towards the square antiprism, that θ for a square antiprism is close to the 'magic' angle of 54.7° where $(3\cos^2\theta - 1)$ changes sign. Therefore square-antiprismatic structures should give small dipolar ^{31}P shifts of either sign, whereas dodecahedral structures should have larger shifts and never change sign.

Examination of the rearrangement path from dodecahedron to square antiprism[4] reveals that only small

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* Here the angle θ is defined as axis–Ln–P, not axis–Ln–S as used to characterise polyhedra in, *e.g.*, ref. 4.

rotations of the ligands are required, but that this changes the direction of the principal symmetry axis by 90°.

Hence, although the present two structures alone give no information about what may be happening in solution, a change from dodecahedron to square antiprism at holmium in solution is in agreement with the n.m.r. data, the prediction of ligand–ligand repulsions, and observations made on the geometry of similar molecules in the solid state. This means that if the ideal structures predominate in solution, then the structures of these easily deformed species in the solid are partly determined by packing considerations. Indeed, the structure of $[Ce(S_2PMe_2)_4]^-$ as its $AsPh_4^+$ salt is also an intermediate structure[7] like the praseodymium analogue[2,4] as its PPh_4^+ salt, but lies at a different place on the rearrangement reaction co-ordinate, as do the two independent cerium molecules. The r.m.s. deviations from the dodecahedron are 0.074 (Ce 1), 0.076 (Ce 2), and 0.084 (Pr) Å, and from the square antiprism 0.097 (Ce 1), 0.120 (Ce 2), and 0.116 (Pr) Å.

Further series of complexes are being investigated both by n.m.r. spectroscopy and *X*-ray crystallography; hence we hope to be able to fully test the above hypothesis.

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