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Dithiophosphinate Complexes of the Lanthanides. Preparation of the Complexes $[Ln\{S_2PR_2\}_4][AsPh_4]$, R = OMe, OPr^i. Determination of the Crystal Structures for Ln = Ce, Er (R = OMe) and Ln = Nd, Ho (R = OPr^i)

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Lanthanide ions react with the salts of the dithiophosphorus acids R_2PS_2H (R = OMe, OPr^i) in the corresponding alcohol to form the tetrakis anionic complexes which may be isolated as their tetraphenylarsonium salts. For R = OPr^i, the complexes of the heavy ions crystallise as solvates, the solvent being easily removed in vacuo. *The crystal structures of the complexes $[Ln\{S_2PR_2\}_4][AsPh_4]$ have been determined from diffractometer data for Ln = Ce and Er, R = OMe; and Ln = Nd and Ho, R = OPr^i.*

$[Ce\{S_2P(OMe)_2\}_4][AsPh_4]$: monoclinic, space group Cc with a = 14.762(3), b = 16.780(4), c = 19.890(3) Å and β = 101.09(1)°, R = 0.041.

$[Er\{S_2P(OMe)_2\}_4][AsPh_4]$: isomorphous to the above with a = 14.626(3), b = 16.760(2), c = 19.718(1) Å and β = 100.89(1)°, R = 0.056.

$[Nd\{S_2P(OPr^i)_2\}_4][AsPh_4]$: monoclinic, space group $P2_1/c$ with a = 12.868(4), b = 24.966(4), c = 21.420(6) Å and β = 102.32(2)°, R = 0.072.

$[Ho\{S_2P(OPr^i)_2\}_4][AsPh_4]\cdot Pr^iOH$: monoclinic, space group $P2_1/n$ with a = 14.401(3), b = 32.427(6), c = 15.168(2) Å and β = 93.46(1)°, R = 0.069. The lanthanide ions are surrounded by eight sulphur atoms (Ce–S = 2.969, Nd–S = 2.984, Ho–S = 2.865, Er–S = 2.856 Å) in an almost perfect D_{2d} dodecahedral arrangement (mmmm isomer). The Ho complex contains a molecule of uncoordinated lattice solvent.

The solid state structures are compared with results obtained from paramagnetic NMR experiments in solution.

Introduction

Although ions of the f transition elements are considered to be hard acids, we have been able to prepare a number of complexes of both the lanthanides and actinides with dithiophosphinate, $R_2PS_2^-$, ligands where the donor atom is sulphur [1–12]. In previous papers we have reported studies on complexes of the type $Ln\{S_2PR_2\}_3$, $[Ln\{S_2PR_2\}_4]^-$, $Th\{S_2PR_2\}_4$, and $UO_2\{S_2PR_2\}_2\cdot L$ where L is an additional monodentate ligand. The interest in these compounds lies in the fact that the sulphur atoms are easily polarisable and that covalent contributions to the bonding between the ligand and the metal ion are more easily measured than for corresponding oxygen donor systems. In our studies to date, we have been able to determine the hyperfine coupling between the unpaired electrons associated with the paramagnetic lanthanide ions and the ^{31}P nuclei in the bound ligands in the complexes $[Ln\{S_2PR_2\}_4]^-$, where R = OEt [5] or Me [11]. The method which we employ to obtain the hyperfine coupling information from the isotropic shifts observed in the NMR spectra of these complexes has already been reported [5, 11]. Using this method of calculation we have been able to demonstrate that a change in solution structure takes place at Dy or Ho with a concommitant change in the hyperfine coupling. We have shown that this change in structure is most probably from dodecahedral to square-antiprismatic in solution, in contrast to the solid where we have observed no analogous structural break [9, 10]. Our results to date indicate that the hyperfine coupling in these compounds is sensitive to the structure, being about twice as large for the dodecahedral ions as for the square-antiprismatic ones. We have also observed that the coupling diminishes when the substituents at phosphorus are less electronegative.

It is of course dangerous to base a hypothesis on the study of only two series of complexes ($[Ln\{S_2PR_2\}_4]^-$ where R = OEt or Me). Hence, in order to confirm these conclusions we have carried out a systematic study of this type of eight coordinate complex, varying the substituents at phosphorus and determining the effect on the solid state structures, on the solution structures and on the hyperfine coupling. In the present paper we report the synthesis and solid state structures for the complexes $[Ln\{S_2PR_2\}_4]^-$ with R = OMe, OPr^i. In the following

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paper we report an NMR study on these series of complexes with the determination of their solution structures and the hyperfine coupling to ^{31}P.

Experimental

The complexes $[AsPh_4][Ln\{S_2PR_2\}_4]$ were prepared in general from the reaction of the hydrated metal chlorides, $NH_4S_2P(OMe)_2$ (FLUKA) or $NaS_2P(OPr^i)_2$ [13], and Ph_4AsCl (FLUKA) in hot methanol or isopropanol. For R = OMe and Ln = Dy–Yb, the anhydrous chlorides were used. The experimental work up was similar to that reported for previous compounds of this type [4], the heavier members being noticeably sensitive to moisture, R = OMe more so than R = OPr^i. All the isolated complexes except for Ln = Yb and R = OMe gave satisfactory elemental analyses which are reported, along with the yields, in Table I. The yellow Yb methoxy complex was isolated and kept under inert (Ar) atmosphere in a sealed tube. However, the yellow colour of these crystals rapidly disappeared, rendering the elemental analysis meaningless. The NMR spectrum was measured by extracting the product with (anhydrous) CD_2Cl_2 from the reaction mixture.

Suitable crystals for X-ray studies were obtained from isopropanol solutions. The air-stable Ce and Nd complexes required no special precautions; however, the crystals of the moisture-sensitive Ho and Er analogues were 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 [14], and a numerical absorption correction applied as reported previously [7]. Crystal data, measurement methods, structure determination and refinement are summarised in Table II. Scattering factors for the neutral atoms were taken from Cromer and Mann [15], and anomalous scattering coefficients from Cromer and Liberman [16]. Computer programs for data reduction and structure solution were taken from the 'XRAY-72' program system [17]. The figure was prepared with the aid of the program ORTEP [18] and the co-ordination polyhedra analysed with the program POLY [19].

The structures of the Ce, Nd and Ho compounds were solved by conventional Patterson and Fourier methods and refined by least squares in three (Ce) or five (Nd, Ho) blocks. The Er complex is isomorphous with the cerium analogue, hence the starting co-ordinates were taken from the previous structure and successfully refined. A final difference Fourier

TABLE I. Analytical Data and Yields for $[AsPh_4][Ln\{S_2PR_2\}_4]$.

Ln	R	C%	H%	S%	P%	Yield%
La	OMe	33.74(33.40)	3.87(3.85)	22.58(22.29)	10.70(10.77)	85
Ce	OMe	33.89(33.36)	3.75(3.85)	22.37(22.26)		79
Pr	OMe	33.50(33.34)	3.90(3.85)	21.90(22.25)		70
Nd	OMe	31.98(33.24)	3.79(3.84)	21.98(22.18)		80
Sm	OMe	32.97(33.07)	3.73(3.82)	21.61(22.06)		68
Eu	OMe	33.20(33.02)	3.62(3.81)	21.74(22.04)		73
Tb	OMe	31.87(32.82)	3.67(3.79)	22.27(21.90)		59
Dy	OMe	32.40(32.72)	3.80(3.78)	21.30(21.87)		38
Ho	OMe	31.07(32.66)	3.59(3.77)	20.90(21.79)		61
Er	OMe	31.20(32.58)	3.53(3.76)	21.31(21.75)		49
Tm	OMe	32.40(32.55)	4.00(3.73)	21.30(21.72)	10.60(10.49)	32
La	OPr^i	42.09(41.92)	5.56(5.57)	18.90(18.66)		83
Ce	OPr^i	41.77(41.88)	5.55(5.56)	19.10(18.63)		91
Pr	OPr^i	41.57(41.86)	5.52(5.56)	18.98(18.62)		86
Nd	OPr^i	41.58(41.76)	5.48(5.55)	18.52(18.58)		85
Sm	OPr^i	41.26(41.57)	5.59(5.52)	19.05(18.50)		89
Eu	OPr^i	41.30(41.52)	5.52(5.52)	18.15(18.48)		89
Gd	OPr^i	40.98(41.37)	5.46(5.50)	18.98(18.40)		88
Tb	OPr^i	41.16(41.32)	5.50(5.49)	18.49(18.38)		88
Dy	OPr^i	41.05(41.21)	5.45(5.48)	18.96(18.34)		75
Ho	OPr^i	42.68(41.14)	5.64(5.47)	18.58(18.30)		76
Er	OPr^i	41.84(41.07)	5.34(5.46)	17.63(18.27)		85
Tm	OPr^i	41.07(41.02)	5.45(5.45)	18.43(18.25)		84
Yb	OPr^i	41.47(40.90)	5.27(5.43)	17.93(18.20)		78
Lu	OPr^i	40.62(40.84)	5.57(5.43)			68

TABLE II. Summary of Crystal Data, Intensity Measurements, Structure Solution and Refinement for $[\text{AsPh}_4][\text{Ln}\{\text{S}_2\text{PR}_2\}_4]$.*

Ln/R	Ce/OMe	Er/OMe	Nd/OPr^i	Ho/OPr^i
Formula	$\text{CeS}_8\text{P}_4\text{AsC}_{32}\text{H}_{44}\text{O}_8$	$\text{ErS}_8\text{P}_4\text{AsC}_{32}\text{H}_{44}\text{O}_8$	$\text{NdS}_8\text{P}_4\text{AsC}_{48}\text{H}_{76}\text{O}_8$	$\text{HoS}_8\text{P}_4\text{AsC}_{51}\text{H}_{84}\text{O}_9$
Molecular weight	1152.1	1179.3	1380.7	1461.5
Crystal dimensions (mm)	0.28 × 0.26 × 0.24	0.28 × 0.26 × 0.17	0.29 × 0.25 × 0.19	0.47 × 0.40 × 0.19
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a (Å)	14.762(3)	14.626(3)	12.868(4)	14.400(3)
b (Å)	16.780(4)	16.760(3)	24.966(4)	32.427(6)
c (Å)	19.890(3)	19.718(2)	21.420(6)	15.167(2)
β (°)	101.09(1)	100.89(1)	102.32(2)	93.46(1)
U (Å^3)	4835(2)	4746(1)	6723(3)	7070(2)
Z	4	4	4	4
d_{calc} (g cm^{-3})	1.58	1.65	1.36	1.38
d_{obsd} (g cm^{-3})	1.57	1.63	1.36	1.37
F_{000}	2316	2356	2836	3000
Space group	Cc	Cc	$P2_1/c$	$P2_1/n$
Radiation	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
λ (Å)	0.71069	0.71069	0.71069	0.71069
μ (cm^{-1})	21.7	30.8	16.7	20.1
Scan method	$2\theta-\theta$	$2\theta-\theta$	$2\theta-\theta$	$2\theta-\theta$
$(\sin\theta/\lambda)_{max}$	0.54	0.70	0.49	0.50
No of unique reflections	3164	5820	6003	5959
No of reflections $< 3\sigma$	324	3584	2680	2628
No of observations/No of variables	11.0 (10.5*)	12.0 (8.3*)	17.0 (13.5*)	16.2 (12.4*)
Structure solution	Patterson & Fourier	Refinement only	Patterson & Fourier	Patterson & Fourier
Refinement method	Blocked matrix least squares	Blocked matrix least squares	Blocked matrix least squares	Blocked matrix least squares
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
w	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$
R	0.041	0.056	0.072	0.069
R_w	0.042	0.053	0.076	0.092
Goodness of fit	3.04	1.16	2.70	1.57

*Only those reflections of $I < 3\sigma$ with $|F_c| > |F_o|$ were included in the refinement. For Ln = Ho, R = OPr^i, the structure is of the isopropanol solvate.

synthesis for the holmium complex revealed a molecule of uncoordinated solvent which was then included in the refinement. The oxygen atom was assigned by analysis of the temperature factors.

Final positional co-ordinates for all the non-hydrogen atoms are reported in Tables III (Ce), IV (Er), V (Nd) and VI (Ho). Derived bond lengths and angles for the four compounds are presented in Table VII and a perspective view of one of the complexes is shown in Fig. 1. The other structures are identical. Tables of observed and calculated structure factors, and thermal parameters, are available as supplementary material.

Discussion

In agreement with previous studies of the reaction of tervalent lanthanide (Ln) ions with dithiophosphinate, $R_2PS_2^-$, ligands, when R is small (OMe, OPr^i), tetrakis eight co-ordinate anionic complexes are formed in alcoholic media [4]. In the present study the alcohol used was methanol or isopropanol, to avoid the formation of any transesterification products. However, this does not appear to be important as the final recrystallisation of the methoxy compounds shows. The $[\text{AsPh}_4]^+$ salts may be isolated by extraction into CH_2Cl_2 followed by recrystallisation from isopropanol. For the light members of the series, the presence of water of hydration in the starting chlorides presented no problems. However, for the heavy ions and the methoxy ligand anhydrous chlorides were used and the reaction carried out in a dry atmosphere as the complexes become progressively more hygroscopic. In contrast, anhydrous chlorides were not necessary with the isopropoxy ligand as the complexes are markedly less moisture-sensitive. Final recrystallisation was carried out under argon.

The isolation of the Yb product with the methoxy ligand poses a problem which we have been unable to resolve. Although the expected yellow product is formed and we were able to obtain its NMR spectrum, the yellow colour rapidly disappears even when the solid is stored under dry argon, hence we report no analytical data for this compound. The colourless product has yet to be fully characterised.

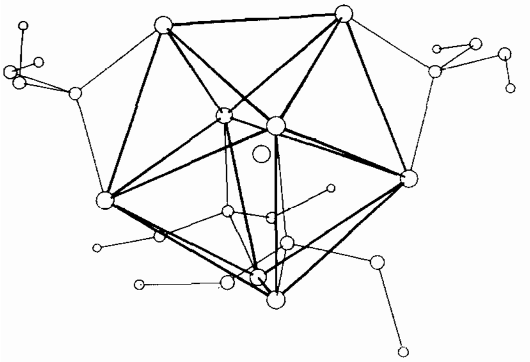

Fig. 1. A perspective view of the complex $[Er\{S_2P(OMe)_2\}_4]^-$ showing the dodecahedral geometry.

TABLE III. Atomic Co-ordinates for $[AsPh_4][Ce\{S_2P(OMe)_2\}_4]$.

Atom	x	y	z
Ce	0	0.23995(4)	0.25
As	0.4324(1)	0.31706(8)	0.11602(6)
P(1)	0.0689(3)	0.4210(2)	0.3352(2)
P(2)	0.2162(2)	0.1429(2)	0.2897(2)
P(3)	−0.0520(3)	0.1766(2)	0.0751(2)
P(4)	−0.2181(3)	0.2150(2)	0.3014(2)
S(1)	0.0619(3)	0.3208(2)	0.3834(2)
S(2)	0.0356(3)	0.4123(2)	0.2349(2)
S(3)	0.1963(3)	0.2395(2)	0.2323(2)
S(4)	0.1093(3)	0.1115(2)	0.3287(2)
S(5)	−0.0452(3)	0.2896(2)	0.1025(2)
S(6)	−0.0357(3)	0.1043(2)	0.1540(2)
S(7)	−0.1942(3)	0.2897(2)	0.2304(2)
S(8)	−0.1087(3)	0.1501(2)	0.3380(2)
C(1)	0.249(1)	0.435(1)	0.3448(8)
C(2)	−0.007(1)	0.563(1)	0.335(1)
C(3)	0.306(1)	0.203(1)	0.4070(8)
C(4)	0.224(2)	−0.002(1)	0.243(1)
C(5)	−0.226(1)	0.146(1)	0.0398(9)
C(6)	0.116(1)	0.172(1)	0.0492(8)
C(7)	−0.218(1)	0.327(1)	0.3943(9)
C(8)	−0.311(1)	0.112(1)	0.2169(9)
C(9)	0.4323(9)	0.2062(7)	0.0952(6)
C(10)	0.4892(9)	0.1767(8)	0.0523(6)
C(11)	0.482(1)	0.0959(9)	0.0383(7)
C(12)	0.430(1)	0.0439(9)	0.0673(8)
C(13)	0.374(1)	0.0743(9)	0.1107(7)
C(14)	0.374(1)	0.1555(9)	0.1252(7)
C(15)	0.5252(9)	0.3670(7)	0.0773(6)
C(16)	0.501(1)	0.4281(9)	0.0256(7)
C(17)	0.577(1)	0.463(1)	−0.0022(8)
C(18)	0.666(1)	0.4370(8)	0.0187(7)
C(19)	0.688(1)	0.3824(9)	0.0694(7)
C(20)	0.616(1)	0.3438(8)	0.0967(7)
C(21)	0.3146(8)	0.3577(7)	0.0785(6)
C(22)	0.287(1)	0.3537(9)	0.0049(7)
C(23)	0.198(1)	0.3840(9)	−0.0248(7)
C(24)	0.140(1)	0.4154(9)	0.0155(7)
C(25)	0.170(1)	0.4187(9)	0.0854(7)
C(26)	0.2557(9)	0.3883(7)	0.1184(6)
C(27)	0.4608(9)	0.3331(8)	0.2123(6)
C(28)	0.482(1)	0.2678(8)	0.2555(8)
C(29)	0.500(1)	0.285(1)	0.3287(8)
C(30)	0.497(1)	0.3637(9)	0.3523(7)
C(31)	0.475(1)	0.4254(9)	0.3084(8)
C(32)	0.4549(9)	0.4110(8)	0.2356(6)
O(1)	0.1642(8)	0.4657(6)	0.3586(5)
O(2)	0.0061(7)	0.4850(6)	0.3650(5)
O(3)	0.3054(7)	0.1506(6)	0.3483(5)
O(4)	0.2520(7)	0.0746(6)	0.2478(5)
O(5)	−0.1423(7)	0.1576(6)	0.0204(4)
O(6)	0.0180(7)	0.1582(5)	0.0254(4)
O(7)	−0.2601(7)	0.2582(6)	0.3596(5)
O(8)	−0.3074(7)	0.1613(6)	0.2755(5)

TABLE IV. Atomic Co-ordinates for $[AsPh_4][Er\{S_2P(OMe)_2\}_4]$.

Atom	x	y	z
Er	0	0.24227(4)	0.25
As	0.4353(2)	0.3179(1)	0.1165(1)
P(1)	0.0702(4)	0.4180(3)	0.3353(3)
P(2)	0.2161(3)	0.1485(3)	0.2864(3)
P(3)	−0.0475(4)	0.1772(3)	0.0794(3)
P(4)	−0.2115(4)	0.2196(3)	0.3001(3)
S(1)	0.0634(4)	0.3154(3)	0.3803(3)
S(2)	0.0375(4)	0.4095(3)	0.2337(3)
S(3)	0.1917(3)	0.2462(3)	0.2302(3)
S(4)	0.1095(4)	0.1175(3)	0.3279(3)
S(5)	−0.0361(4)	0.2908(3)	0.1059(3)
S(6)	−0.0341(5)	0.1100(3)	0.1618(3)
S(7)	−0.1794(4)	0.2955(3)	0.2304(3)
S(8)	−0.1028(4)	0.1532(3)	0.3361(3)
C(1)	0.253(1)	0.437(1)	0.344(1)
C(2)	−0.004(2)	0.561(1)	0.332(2)
C(3)	0.309(2)	0.206(1)	0.404(1)
C(4)	0.229(2)	0.001(1)	0.244(2)
C(5)	−0.220(2)	0.147(2)	0.042(2)
C(6)	0.122(2)	0.168(1)	0.052(1)
C(7)	−0.206(2)	0.336(1)	0.393(1)
C(8)	−0.302(2)	0.117(2)	0.216(1)
C(9)	0.441(1)	0.208(1)	0.0939(8)
C(10)	0.498(1)	0.174(1)	0.0535(9)
C(11)	0.494(2)	0.095(1)	0.039(1)
C(12)	0.441(1)	0.046(1)	0.067(1)
C(13)	0.383(2)	0.074(1)	0.111(1)
C(14)	0.385(1)	0.157(1)	0.128(1)
C(15)	0.532(1)	0.367(1)	0.0769(8)
C(16)	0.508(1)	0.426(1)	0.028(1)
C(17)	0.583(2)	0.461(1)	−0.005(1)
C(18)	0.673(2)	0.437(1)	0.018(1)
C(19)	0.695(1)	0.380(1)	0.072(1)
C(20)	0.624(2)	0.345(1)	0.099(1)
C(21)	0.320(1)	0.361(1)	0.0805(9)
C(22)	0.293(2)	0.352(1)	0.005(1)
C(23)	0.206(2)	0.380(1)	−0.029(1)
C(24)	0.148(1)	0.415(1)	0.014(1)
C(25)	0.172(2)	0.421(1)	0.086(1)
C(26)	0.262(2)	0.394(1)	0.118(1)

(continued on facing page)

TABLE IV *(continued)*

Atom	x	y	z
C(27)	0.468(1)	0.337(1)	0.2139(8)
C(28)	0.487(2)	0.267(1)	0.256(1)
C(29)	0.505(2)	0.286(1)	0.332(1)
C(30)	0.504(2)	0.366(1)	0.355(1)
C(31)	0.483(2)	0.429(1)	0.308(1)
C(32)	0.462(1)	0.414(1)	0.2393(9)
O(1)	0.167(1)	0.4642(8)	0.3601(7)
O(2)	0.004(1)	0.4816(9)	0.3641(7)
O(3)	0.3108(9)	0.1565(7)	0.3429(7)
O(4)	0.251(1)	0.0807(8)	0.2406(8)
O(5)	−0.139(1)	0.1576(9)	0.0251(7)
O(6)	0.023(1)	0.1552(8)	0.0296(6)
O(7)	−0.2509(9)	0.2645(8)	0.3600(7)
O(8)	−0.3025(9)	0.1701(8)	0.2729(9)

TABLE V. Atomic Co-ordinates for $[AsPh_4][Nd\{S_2P(OPr^i)_2\}_4]$.

Atom	x	y	z
Nd	0.42547(8)	0.14389(4)	0.23404(4)
As	0.8187(2)	0.43585(7)	0.06891(8)
P(1)	0.3339(4)	0.0100(2)	0.2008(2)
P(2)	0.1838(4)	0.2110(2)	0.1677(2)
P(3)	0.6686(5)	0.1225(2)	0.1868(2)
P(4)	0.5051(5)	0.2202(2)	0.3747(3)
S(1)	0.3499(4)	0.0621(2)	0.1341(2)
S(2)	0.3700(4)	0.0412(2)	0.2873(2)
S(3)	0.2054(4)	0.1645(2)	0.2452(2)
S(4)	0.3142(4)	0.2175(2)	0.1348(2)
S(5)	0.5551(4)	0.1696(2)	0.1400(2)
S(6)	0.6406(4)	0.0997(2)	0.2707(2)
S(7)	0.4678(5)	0.1448(2)	0.3763(2)
S(8)	0.4923(5)	0.2493(2)	0.2880(2)
C(1)	0.178(2)	−0.054(1)	0.131(1)
C(2)	0.109(3)	−0.021(1)	0.097(1)
C(3)	0.088(3)	−0.077(1)	0.163(2)
C(4)	0.510(2)	−0.0429(8)	0.1904(9)
C(5)	0.575(2)	−0.0530(9)	0.258(1)
C(6)	0.519(2)	−0.0893(9)	0.146(1)
C(7)	0.190(2)	0.311(1)	0.230(1)
C(8)	0.113(2)	0.319(1)	0.266(1)
C(9)	0.222(2)	0.349(1)	0.185(1)
C(10)	0.080(2)	0.1374(7)	0.0835(8)
C(11)	−0.027(2)	0.1144(8)	0.0902(9)
C(12)	0.087(2)	0.1510(9)	0.015(1)
C(13)	0.698(2)	0.063(1)	0.090(1)
C(14)	0.607(2)	0.0551(9)	0.042(1)
C(15)	0.762(2)	0.009(1)	0.097(1)
C(16)	0.804(1)	0.2012(7)	0.2246(8)
C(17)	0.832(2)	0.2361(8)	0.1708(9)
C(18)	0.901(2)	0.1897(8)	0.2793(9)
C(19)	0.348(3)	0.273(1)	0.410(1)
C(20)	0.363(2)	0.3244(9)	0.462(1)
C(21)	0.286(2)	0.237(1)	0.442(1)
C(22)	0.685(2)	0.274(1)	0.418(1)
C(23)	0.775(3)	0.263(1)	0.397(1)
C(24)	0.711(2)	0.290(1)	0.492(1)
C(25)	0.920(1)	0.4750(6)	0.1332(7)
C(26)	1.029(1)	0.4692(6)	0.1315(7)
C(27)	1.103(2)	0.4991(7)	0.1785(8)
C(28)	1.064(2)	0.5343(7)	0.2208(8)
C(29)	0.956(2)	0.5401(7)	0.2171(8)
C(30)	0.878(1)	0.5108(7)	0.1732(8)
C(31)	0.898(1)	0.3918(7)	0.0227(8)
C(32)	0.941(2)	0.3447(7)	0.0526(8)
C(33)	1.012(2)	0.3149(8)	0.018(1)
C(34)	1.029(2)	0.3336(8)	−0.040(1)
C(35)	0.986(2)	0.3815(9)	−0.0667(9)
C(36)	0.916(2)	0.4112(7)	−0.0372(9)
C(37)	0.732(2)	0.4848(8)	0.0116(8)
C(38)	0.658(2)	0.464(1)	−0.035(1)
C(39)	0.588(2)	0.503(1)	−0.074(1)
C(40)	0.596(2)	0.556(1)	−0.064(1)
C(41)	0.686(3)	0.577(1)	−0.022(2)
C(42)	0.761(2)	0.538(1)	0.018(1)
C(43)	0.725(1)	0.3885(7)	0.1039(8)
C(44)	0.727(2)	0.3947(8)	0.1695(9)
C(45)	0.650(2)	0.3611(8)	0.1924(9)
C(46)	0.584(2)	0.3245(8)	0.149(1)
C(47)	0.593(2)	0.3194(8)	0.0853(9)
C(48)	0.664(2)	0.3522(8)	0.0605(8)
O(1)	0.216(1)	−0.0148(4)	0.1909(5)
O(2)	0.398(1)	−0.0443(5)	0.1965(5)
O(3)	0.134(1)	0.2667(5)	0.1797(5)
O(4)	0.0815(9)	0.1925(4)	0.1144(5)
O(5)	0.684(1)	0.0678(6)	0.1492(8)
O(6)	0.783(1)	0.1496(5)	0.1929(6)
O(7)	0.450(2)	0.2546(8)	0.4229(9)
O(8)	0.628(1)	0.2256(6)	0.4182(6)

TABLE VI. Atomic Co-ordinates for $[AsPh_4][Ho\{S_2P(OPr^i)_2\}_4]\cdot Pr^iOH$.

Atom	x	y	z
Ho	0.08798(8)	0.13848(3)	0.16539(5)
As	0.2426(2)	0.35539(7)	0.0683(1)
P(1)	−0.1264(5)	0.1087(2)	0.0786(3)
P(2)	0.2574(5)	0.0961(2)	0.3108(3)
P(3)	0.1930(5)	0.1280(2)	−0.0336(3)
P(4)	0.0475(4)	0.2179(2)	0.3102(3)
S(1)	−0.0555(4)	0.0769(2)	0.1709(3)
S(2)	−0.0720(5)	0.1636(2)	0.0608(3)
S(3)	0.2684(4)	0.1487(2)	0.2484(3)
S(4)	0.1424(4)	0.0671(2)	0.2741(3)
S(5)	0.1353(5)	0.0827(2)	0.0322(3)
S(6)	0.1803(5)	0.1807(2)	0.0286(3)
S(7)	0.0919(4)	0.2269(2)	0.1911(3)
S(8)	0.0026(4)	0.1604(2)	0.3233(3)
C(1)	−0.137(2)	0.0417(8)	−0.023(1)
C(2)	−0.098(2)	0.0308(9)	−0.110(2)
C(3)	−0.240(2)	0.0283(9)	−0.028(2)
C(4)	−0.261(2)	0.1235(9)	0.187(2)
C(5)	−0.299(2)	0.165(1)	0.186(2)
C(6)	−0.330(3)	0.088(1)	0.209(2)
C(7)	0.350(3)	0.024(1)	0.312(2)
C(8)	0.389(2)	0.004(1)	0.243(2)

(continued overleaf)

TABLE VI *(continued)*

Atom	x	y	z
C(9)	0.427(3)	0.024(1)	0.398(2)
C(10)	0.211(2)	0.1260(8)	0.463(1)
C(11)	0.144(2)	0.0994(7)	0.507(1)
C(12)	0.281(2)	0.1485(9)	0.534(2)
C(13)	0.364(2)	0.1118(8)	0.025(1)
C(14)	0.416(2)	0.071(1)	0.005(2)
C(15)	0.433(3)	0.147(1)	0.017(2)
C(16)	0.055(2)	0.133(1)	−0.167(2)
C(17)	0.039(2)	0.105(1)	−0.240(2)
C(18)	0.054(3)	0.177(1)	−0.193(2)
C(19)	0.174(2)	0.2659(7)	0.387(1)
C(20)	0.157(2)	0.2869(8)	0.476(1)
C(21)	0.277(2)	0.2560(8)	0.382(2)
C(22)	−0.115(2)	0.2532(8)	0.283(1)
C(23)	−0.198(2)	0.2447(9)	0.341(2)
C(24)	−0.124(3)	0.295(1)	0.239(2)
C(25)	0.190(2)	0.3664(7)	0.181(1)
C(26)	0.248(2)	0.3672(7)	0.254(1)
C(27)	0.214(2)	0.3757(8)	0.337(1)
C(28)	0.120(2)	0.3843(8)	0.336(1)
C(29)	0.059(2)	0.3854(8)	0.264(2)
C(30)	0.093(2)	0.3746(7)	0.184(1)
C(31)	0.333(2)	0.3128(6)	0.085(1)
C(32)	0.316(2)	0.2789(7)	0.140(1)
C(33)	0.382(2)	0.2478(7)	0.152(1)
C(34)	0.468(2)	0.2519(7)	0.118(1)
C(35)	0.486(2)	0.2862(8)	0.065(1)
C(36)	0.422(2)	0.3170(7)	0.052(1)
C(37)	0.300(2)	0.4046(6)	0.026(1)
C(38)	0.311(2)	0.4371(7)	0.083(1)
C(39)	0.360(2)	0.4741(8)	0.052(2)
C(40)	0.391(2)	0.4746(8)	−0.032(2)
C(41)	0.377(2)	0.4389(7)	−0.088(1)
C(42)	0.328(2)	0.4040(7)	−0.059(1)
C(43)	0.145(2)	0.3396(7)	−0.013(1)
C(44)	0.097(2)	0.3692(8)	−0.059(1)
C(45)	0.013(2)	0.3578(9)	−0.115(2)
C(46)	−0.008(2)	0.316(1)	−0.122(2)
C(47)	0.040(2)	0.2851(9)	−0.075(2)
C(48)	0.122(2)	0.2968(8)	−0.016(1)
C(49)	0.286(3)	0.045(1)	0.741(2)
C(50)	0.346(3)	0.031(1)	0.658(2)
C(51)	0.241(3)	0.024(1)	0.796(3)
O(1)	−0.133(1)	0.0866(4)	−0.0130(8)
O(2)	−0.232(1)	0.1121(4)	0.0972(8)
O(3)	0.350(1)	0.0691(5)	0.2943(9)
O(4)	0.276(1)	0.1002(4)	0.4158(7)
O(5)	0.298(1)	0.1176(4)	−0.0526(8)
O(6)	0.158(1)	0.1284(4)	−0.1358(8)
O(7)	0.123(1)	0.2268(4)	0.3860(7)
O(8)	−0.030(1)	0.2515(4)	0.3338(7)
O(9)	0.327(2)	0.0845(8)	0.756(1)

Although the initial syntheses were carried out without regard to crystal quality, it was observed that a number of the heavy ions gave crystals of the isopropoxy complex that became opaque when dried *in vacuo.* No attention was paid to this as the elemental analyses and NMR properties were as expected. However, crystals dried in this manner proved to be unsuitable for X-ray analysis although this was not the case for the light ions (Nd). Crystals of the Ho analogue were dried with paper tissue fibres and found to remain transparent and to give sharp Bragg peaks. The result of the crystal structure determination allows us to offer a simple explanation for this behaviour.

The crystals form with one molecule of lattice solvent per asymmetric unit. This uncoordinated solvent is not strongly bound, and under moderate pumping may be removed, thus destroying the crystal lattice. As all compounds were routinely dried *in vacuo*, the solvent was never seen in the NMR spectra and was not present in the samples sent for elemental analysis.

The crystal structures confirm that the lanthanide ions are coordinated to eight sulphur atoms. The average Ln–S bond lengths are 2.969 (Ce), 2.948 (Nd), 2.865 (Ho) and 2.856 Å (Er), decreasing as expected with the lanthanide contraction. Previously reported structures of this type, $[\mathrm{Ln}\{S_2PR_2\}_4]^-$, have given values for Ln–S of 2.991, 2.976 and 2.870 Å (R = Me, and Ln = Ce, Pr and Tm) [1, 10], and 2.989 and 2.858 Å (R = OEt, and Ln = La and Er) [9], whereas the bonds are shorter, 2.788, 2.741 and 2.692 Å, in the six co-ordinate species $\mathrm{Ln}\{S_2PR_2\}_3$ (R = C_6H_{11}, Ln = Sm, Dy and Lu) [3, 7].

The four membered chelate rings have generally been observed to be close to planar, although significant distortions from planarity [10] are known. In the two structures with R = OMe they are only slightly distorted, the deviations from planarity being measured as the fold about the S···S direction varying from 0.8 to 7.9°. With R = OPr^i, the distortions are more important, varying from 0.9 to 16.1°. The geometry of the chelate rings again shows that the angles at sulphur are always close to 90°, the main variations due to the change in ionic radius being the Ln–S bond length and the bidentate angle at the metal [10]. The isopropoxy groups are rather poorly defined, as is the molecule of lattice solvent.

It has been previously calculated by Blight and Kepert [20] that complexes of this type should fall into two structure types. For $M(\text{bidentate})_4$ systems the most stable polyhedron depends on the normalised bite, b, of the ligand (in the present case b is the intraligand S···S distance divided by the metal–sulphur bond length). For $b < 1.00$ the most stable geometry is the D_{2d} dodecahedron (mmmm isomer), and for $1.00 < b < 1.15$ a smooth change to the D_2 square antiprism (ssss isomer) is predicted. In the present structures b = 1.10 (Ce), 1.11 (Nd), 1.14 (Ho) and 1.14 (Er), and an intermediate structure might well be expected.

In previous studies we have observed both intermediate structures and almost perfect dodecahedra, but we have yet to observe a square antiprism in the

TABLE VII. Bond Lengths (Å) and Angles (°) for $[AsPh_4][Ln\{S_2PR_2\}_4]$ with Estimated Standard Deviations in Parentheses.*

	Ce/OMe	Er/OMe	Nd/OPr^i	Ho/OPr^i
a) Distances				
Ln–S(1)	2.963(3)	2.840(6)	2.968(4)	2.879(6)
Ln–S(2)	2.965(4)	2.885(5)	2.955(5)	2.837(6)
Ln–S(3)	2.985(4)	2.903(6)	2.939(5)	2.838(6)
Ln–S(4)	2.954(4)	2.893(5)	2.939(5)	2.921(5)
Ln–S(5)	2.999(3)	2.906(6)	2.947(6)	2.825(6)
Ln–S(6)	2.953(4)	2.804(6)	2.927(6)	2.877(6)
Ln–S(7)	2.938(4)	2.729(6)	2.979(5)	2.895(6)
Ln–S(8)	2.998(4)	2.887(6)	2.928(5)	2.847(5)
P(1)–S(1)	1.949(5)	1.945(8)	1.977(7)	1.973(8)
P(1)–S(2)	1.966(5)	1.975(7)	1.972(6)	1.971(9)
P(2)–S(3)	1.972(5)	1.971(7)	1.997(7)	1.961(8)
P(2)–S(4)	1.960(5)	1.964(8)	1.960(8)	1.956(9)
P(3)–S(5)	1.971(5)	1.973(7)	1.974(7)	1.985(8)
P(3)–S(6)	1.962(5)	1.957(7)	1.990(8)	1.965(8)
P(4)–S(7)	1.970(6)	1.993(8)	1.946(8)	1.973(7)
P(4)–S(8)	1.967(5)	1.961(7)	1.968(7)	1.987(8)
P(1)–O(1)	1.58(1)	1.61(1)	1.61(1)	1.56(1)
P(1)–O(2)	1.61(1)	1.61(2)	1.60(1)	1.57(2)
P(2)–O(3)	1.587(9)	1.61(1)	1.58(1)	1.62(2)
P(2)–O(4)	1.57(1)	1.60(2)	1.62(1)	1.60(1)
P(3)–O(5)	1.581(9)	1.58(1)	1.62(2)	1.60(2)
P(3)–O(6)	1.59(1)	1.60(2)	1.60(2)	1.60(1)
P(4)–O(7)	1.59(1)	1.60(2)	1.62(2)	1.56(1)
P(4)–O(8)	1.60(1)	1.57(1)	1.66(2)	1.61(2)
S(1)·····S(2)	3.286(5)	3.252(7)	3.279(6)	3.273(8)
S(3)·····S(4)	3.299(5)	3.268(7)	3.273(8)	3.244(8)
S(5)·····S(6)	3.269(5)	3.223(7)	3.282(7)	3.243(8)
S(7)·····S(8)	3.258(5)	3.226(7)	3.277(7)	3.262(8)
b) Angles				
S(1)–Ln–S(2)	67.31(9)	69.2(1)	67.2(1)	69.9(2)
S(1)–Ln–S(3)	88.1(1)	87.3(2)	90.4(1)	135.0(2)
S(1)–Ln–S(4)	79.4(1)	77.2(2)	82.8(1)	66.6(2)
S(1)–Ln–S(5)	136.1(1)	137.0(2)	78.6(1)	77.3(2)
S(1)–Ln–S(6)	156.6(1)	153.1(2)	94.6(1)	135.6(1)
S(1)–Ln–S(7)	96.5(1)	97.4(2)	134.7(1)	133.8(2)
S(1)–Ln–S(8)	79.3(1)	79.0(2)	157.8(1)	78.6(2)
S(2)–Ln–S(3)	78.2(1)	75.8(2)	78.7(1)	154.9(2)
S(2)–Ln–S(4)	132.5(1)	131.6(2)	134.5(1)	136.4(2)
S(2)–Ln–S(5)	68.90(9)	67.8(1)	132.2(1)	90.4(2)
S(2)–Ln–S(6)	134.38(9)	135.6(2)	82.1(2)	81.7(2)
S(2)–Ln–S(7)	84.1(1)	82.2(2)	67.6(1)	78.4(2)
S(2)–Ln–S(8)	132.4(1)	134.3(2)	134.6(1)	91.2(2)
S(3)–Ln–S(4)	67.5(1)	68.6(2)	67.7(1)	68.6(2)
S(3)–Ln–S(5)	85.6(1)	82.2(2)	135.5(1)	97.9(2)
S(3)–Ln–S(6)	88.8(1)	89.9(2)	156.5(1)	79.3(2)
S(3)–Ln–S(7)	158.3(1)	154.2(2)	83.4(2)	79.3(2)
S(3)–Ln–S(8)	135.1(1)	135.6(1)	91.0(1)	91.6(2)
S(4)–Ln–S(5)	135.8(1)	134.5(2)	68.2(1)	80.1(2)
S(4)–Ln–S(6)	78.0(1)	76.9(2)	135.7(2)	131.6(2)
S(4)–Ln–S(7)	134.2(1)	137.1(2)	133.6(2)	135.0(1)
S(4)–Ln–S(8)	67.8(1)	67.2(2)	77.3(1)	80.7(2)
S(5)–Ln–S(6)	66.6(1)	68.7(2)	67.9(1)	69.3(2)
S(5)–Ln–S(7)	76.3(1)	77.1(2)	133.7(2)	136.6(2)
S(5)–Ln–S(8)	131.9(1)	134.5(2)	85.0(1)	153.6(2)
S(6)–Ln–S(7)	94.9(1)	96.7(2)	76.9(2)	67.7(2)
S(6)–Ln–S(8)	86.6(1)	84.5(2)	93.0(2)	136.9(2)
S(7)–Ln–S(8)	66.6(1)	70.0(2)	67.4(1)	69.2(2)

(continued overleaf)

TABLE VII *(continued)*

	Ce/OMe	Er/OMe	Nd/OPr^i	Ho/OPr^i
Ln–S(1)–P(1)	89.5(2)	90.3(2)	90.0(2)	87.6(3)
Ln–S(2)–P(1)	89.1(2)	88.4(2)	90.5(2)	88.8(3)
Ln–S(3)–P(2)	88.5(2)	89.0(2)	90.0(2)	90.8(3)
Ln–S(4)–P(2)	89.6(2)	89.5(2)	90.7(2)	88.5(3)
Ln–S(5)–P(3)	89.6(1)	88.9(2)	89.4(2)	90.7(3)
Ln–S(6)–P(3)	91.1(2)	92.2(2)	89.6(2)	89.6(3)
Ln–S(7)–P(4)	91.7(2)	92.2(2)	88.9(2)	88.3(2)
Ln–S(8)–P(4)	89.9(2)	88.3(3)	90.0(2)	89.4(2)
S(1)–P(1)–S(2)	114.1(2)	112.1(3)	112.3(3)	112.2(4)
S(1)–P(1)–O(1)	113.1(4)	113.9(6)	113.5(5)	113.1(6)
S(1)–P(1)–O(2)	107.8(4)	109.8(7)	112.4(5)	112.1(6)
S(2)–P(1)–O(1)	111.6(4)	111.9(6)	107.5(5)	107.3(6)
S(2)–P(1)–O(2)	112.1(4)	111.0(6)	111.5(5)	111.0(7)
O(1)–P(1)–O(2)	96.8(6)	97.3(8)	98.9(7)	100.5(8)
S(3)–P(2)–S(4)	114.1(2)	112.3(3)	111.6(3)	111.8(4)
S(3)–P(2)–O(3)	111.7(4)	111.2(5)	111.4(5)	107.7(7)
S(3)–P(2)–O(4)	108.7(4)	108.5(6)	111.7(5)	113.2(6)
S(4)–P(2)–O(3)	110.5(4)	112.3(6)	113.5(6)	112.6(7)
S(4)–P(2)–O(4)	113.2(5)	114.4(6)	113.6(5)	114.1(6)
O(3)–P(2)–O(4)	97.6(5)	97.1(7)	93.9(6)	96.3(7)
S(5)–P(3)–S(6)	112.4(2)	110.2(3)	111.8(4)	110.4(3)
S(5)–P(3)–O(5)	112.0(4)	113.4(6)	113.9(6)	111.5(6)
S(5)–P(3)–O(6)	110.7(4)	110.7(6)	111.0(6)	112.1(6)
S(6)–P(3)–O(5)	112.6(4)	112.5(6)	105.8(7)	112.8(6)
S(6)–P(3)–O(6)	112.5(4)	113.7(6)	112.8(5)	115.1(6)
O(5)–P(3)–O(6)	95.5(5)	95.7(8)	101.0(8)	94.2(8)
S(7)–P(4)–S(8)	111.7(2)	109.3(4)	113.7(3)	110.9(3)
S(7)–P(4)–O(7)	112.4(4)	112.0(6)	111.0(8)	113.3(6)
S(7)–P(4)–O(8)	112.2(4)	113.3(7)	106.1(6)	111.6(5)
S(8)–P(4)–O(7)	112.9(4)	112.4(6)	116.5(7)	108.5(6)
S(8)–P(4)–O(8)	112.0(4)	113.5(6)	112.3(7)	112.3(6)
O(7)–P(4)–O(8)	94.5(6)	95.8(8)	95.4(9)	99.8(7)

*OMe groups: O–C 1.30(3)–1.48(3) Å, P–O–C 117(2)–127(1)°. OPr^i groups: O–C, 1.32(4)–1.60(3) Å; C–C, 1.30(4)–1.68(4) Å; P–O–C, 117(1)–127(2)°; O–C–C, 90(2)–117(3)°; C–C–C, 90(3)–126(3)°. Ph groups: C–C 1.32(2)–1.52(2) Å, C–C–C 112(2)–128(2)°. Isopropanol: O–C, 1.41(5) Å; C–C, 1.29(6), 1.65(5) Å; O–C–C, 98(3)°. $[Ph_4As]^+$ groups: As–C, 1.85(2)–1.95(2) Å; C–As–C, 104.4(8)–114.1(7)°.

solid state. In solution [21] it is clear from paramagnetic NMR data that there is a structural change at Ho in both series of complexes, and the data are in accord with a change from dodecahedral to square antiprismatic. For these reasons we have carefully analysed the co-ordination polyhedra for the four structures presented here. The analysis was carried out by the program POLY [19] based on the least squares method proposed by Dollase [22].

All of the polyhedra were found to be best described as D_{2d} dodecahedra. The calculated root mean square (r.m.s) deviations from the ideal polyhedron are 0.050 (Ce), 0.034 (Nd), 0.029 (Ho) and 0.046 (Er). These deviations are of the same order of magnitude as those found for $[Ln\{S_2P(OEt)_2\}_4]^-$ [9]—0.039 (La) and 0.029 (Er)— but smaller than for $[Ln\{S_2PMe_2\}_4]^-$ [1, 10]—0.075 (Ce), 0.084 (Pr) and 0.069 (Tm)—where a significant distortion towards a D_2 square antiprism was observed. From the few structures of this type known, it seems that alkoxy substituents at phosphorus favour the dodecahedron, whereas alkyl substituents favour the intermediate structure. As the energy difference between the two polyhedra is expected to be small, it would be of interest to investigate the influence of packing forces on the polyhedra by changing the counter ion. Although we have determined structures in a number of different crystal systems, the counter ion has always been tetrahedral, either $[Ph_4P]^+$ or $[Ph_4As]^+$, hence a planar counter ion for example could conceivably change the coordination polyhedron.

The point symmetry of the ideal polyhedron, D_{2d}, means that there are two different co-ordination sites, A and B. It has been frequently observed that the $M–L_A$ bond length is longer than $M–L_B$.

Although this is so for the Ho complex where the A sites are occupied by S(1), S(4), S(6) and S(7), and the B sites by S(2), S(3), S(5) and S(8), it is only so on average for the other structures. For the Ce and Er compounds, the A sites are occupied by S(2), S(4), S(5) and S(8), and the B sites by S(1), S(3), S(6) and S(7) however S(3) and S(4) do not obey the rule. In the Nd complex the A sites are occupied by S(2), S(4), S(5) and S(7), and the B sites by S(1), S(3), S(6) and S(8), and S(1) and S(2) do not conform. In previous dodecahedral structures of this type we have observed a regular behaviour, irregular bond lengths only being found for the intermediate geometries [10]. The $[AsPh_4]^+$ counter ions are tetrahedral as expected.

As our justification for carrying out these four structure determinations rests largely on the observation of two structure types in solution by paramagnetic NMR, a short comment will be made here concerning these results. First, the NMR experiment shows that the series of complexes fall into two structure types in solution, the break occurring at Ho [21]. For this reason the present structures were determined to be characteristic of the solid state before (Ce and Nd) and after (Ho and Er) holmium. The identical structures observed thus show that the solid and solution states have different structural behaviours.

The argument concerning the solution structures rests on the observation of a large relative ^{31}P dipolar shift for the light ions and a small one for the heavy ones. We have previously discussed this phenomenon for the series $[Ln\{S_2PMe_2\}_4]^-$ [10] and $[Ln\{S_2P(OEt)_2\}_4]^-$ [9] and shown that the determining factor in these observations is the angle θ between the Ln–P vector and the fourfold inversion axis of the dodecahedron or the pseudo-eightfold inversion axis of the corresponding square-antiprism (the relative magnitudes of the ^{31}P dipolar shifts depend on the value of $(3\cos^2\theta - 1)$). The values of θ in the present case, ~68° and ~50° again indicate that the solution results are in accord with a change from dodecahedral to antiprismatic *i.e.* a large value of $(3\cos^2\theta - 1)$ to a small one.

The full discussion of these observations is presented elsewhere, along with the NMR results [21].

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