Dithiophosphinate Complexes of the Actinides. Part 1. Preparation and Characterisation of Complexes of Thorium(IV) and the Crystal Structures of $[Th(S_2PR_2)_4]$, R = Me or C_6H_{11} [†]

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Reaction of dithiophosphinate salts with hydrated $ThCl_4$ in the ratio 4 : 1 in ethanolic solution yields the complexes $[Th(S_2PR_2)_4]$ where R = Me, Et, Pr^i, Ph, C_6H_{11}, OEt, or OPr^i. The air-stable complexes have been characterised by their elemental analyses, i.r., and n.m.r. spectra, and the crystal structures have been determined for R = Me and C_6H_{11}. Crystals of $[Th(S_2PMe_2)_4]$ are tetragonal, space group $P4_22_12$, with $a = 10.521(1)$ and $c = 11.936(1)$ Å ($R = 0.030$). Crystals of $[Th\{S_2P(C_6H_{11})_2\}_4]$ are monoclinic, space group $C2/c$, with $a = 42.521(5)$, $b = 11.754(2)$, $c = 23.945(2)$ Å, and $\beta = 100.285(8)°$ ($R = 0.048$). The thorium atoms are surrounded by eight sulphur atoms (av. Th–S = 2.910 Å) in a dodecahedral arrangement (the methyl compound having crystallographic 222 symmetry). In both cases the $M(L–L)_4$ *mmmm* isomer is formed.

DITHIOPHOSPHINATE (S_2PR_2) complexes of the lanthanides have been well investigated over the past five years.[1-4] Due to their relative ease of preparation and stability compared to, for example, the air-sensitive dithiocarbamates (S_2CNR_2) they have proven useful in the investigation of the bonding interaction between hard A-type metal ions and polarisable sulphur-donor B-type ligands.

The existence of a covalent interaction between the lanthanide and the ligand has been demonstrated by n.m.r. methods, and the non-direct participation of the 4*f* orbitals in the bonding confirmed.[5] The presence of the ^{31}P nucleus close to the metal is a convenient n.m.r. probe and is a further advantage of S_2PR_2 over S_2CNR_2 complexes.

The actinides (An) may be considered to have a softer character than the lanthanides (Ln), and the 5*f* orbitals are more easily accessible for bonding than the 4*f* orbitals, hence the comparison of An–S and Ln–S bonding parameters is of considerable interest.

To our knowledge, few S_2PR_2 compounds of the actinides are known, the majority being uranyl mixed-ligand complexes with phosphine oxides.[6a] Complexes of the type $[UO_2(S_2PR_2)_2]$ have been briefly reported for R = Me,[6b] Ph,[6c] and aryl.[6d] The only thorium complex reported to date is $[Th(S_2PR_2)_4]$ for R = Ph.[6c] We note that some diethyldithiocarbamate complexes of the actinides are known,[7] but these are extremely air-sensitive. The structures have been determined for $[Np(S_2CNEt_2)_4]^-$, $[Pu(S_2CNEt_2)_4]^-$, and $[Th(S_2CNEt_2)_4]$. In all cases the metal is co-ordinated by eight sulphur atoms, the ligands spanning the *m* edges of a dodecahedron.[7] We have thus extended our previous studies to the actinides in the hope that the S_2PR_2 complexes will be more stable than their S_2CNR_2 analogues as was found for the lanthanides.

The fluxional behaviour of high co-ordination numbers in solution [8] and the study of the rearrangement reaction co-ordinate frozen in the solid state [9] have become of increasing interest in recent years. As it is to be expected that these [M(bidentate ligand)$_4$] species should lie on the D_{2d} dodecahedron–D_2 square antiprism reaction co-ordinate, it seemed reasonable to carry out a structural investigation of this class of compound, especially in view of the paucity of structural data on actinide *S*-donor ligand complexes.[7]

In this paper, the first part of the series, we report our results on the system $[Th(S_2PR_2)_4]$.

EXPERIMENTAL

Solvents were purified by standard techniques.[10] The compound $ThCl_4{\cdot}8H_2O$ (K and K) was used as supplied. Dithiophosphinate salts were prepared by literature methods [11] and their purity confirmed by elemental analysis and n.m.r. spectroscopy. Infrared spectra were recorded as Nujol mulls with a PE 577 spectrometer. Hydrogen-1 n.m.r. spectra were recorded in CD_2Cl_2 solution with a Bruker WP 60 (60 MHz), WH 80 (80 MHz), or WVH 360 (360 MHz) instrument and chemical shifts are reported relative to $SiMe_4$. Thorium was determined by edta (ethylenediaminetetra-acetate) titration in aqueous ethanol with xylenol orange as indicator at pH *ca.* 1. Elemental analyses (C, H, and S) were carried out by Herrn W. Manzer, ETH, Zurich.

Syntheses.[‡]—(*i*) $[Th(S_2PR_2)_4]$ (R = Me, Et, Pr^i,[§] Ph, *or* C_6H_{11}).[¶] Ethanolic solutions of $ThCl_4{\cdot}8H_2O$ (1 mol) and $M[S_2PR_2]$ (4 mol), where R = Me, Et, Pr^i, Ph, or C_6H_{11} and M = Na^+ or NH_4^+, were stirred for *ca.* 20 min at *ca.* 50 °C. The white suspension was reduced to dryness and the complexes extracted from the $[NH_4]Cl$ or NaCl residue with CH_2Cl_2. The complexes were recrystallized by dissolving in the minimum volume of CH_2Cl_2, adding ethanol dropwise until the appearance of a faint turbidity, and leaving to crystallize overnight. The adducts were filtered on glass sinters, washed with ethanol and diethyl ether, and vacuum dried. They were obtained as well defined, non-hygroscopic, white crystalline solids which were stable for some weeks in the atmosphere. Yields were 20—34%.

[†] Presented in part at the XXI International Conference on Co-ordination Chemistry, Toulouse, 1980.

[‡] All manipulations were carried out in dry atmospheres but no special precautions to exclude oxygen were used.

[§] The isopropyl adduct required more stringently dry conditions than other compounds. The crude adduct was an oil which crystallized from ethanol.

[¶] Anhydrous $ThCl_4$ was used, as the hydrated salt gave a product of uncertain stoicheiometry under the described reaction conditions. Repeated crystallization of this adduct gave essentially unchanged analyses with the C : H : S ratio remaining at 6 : 11 : 1 however, an unidentified impurity was observed in the ^1H n.m.r. spectrum (triplet, $\delta = 4.41$).

(*ii*) [$Th(S_2PR_2)_4$] (R = OEt *or* OPr^i). A similar preparative method to (*i*) was employed except that syntheses were performed in ethanol (for the ethoxy-compound) and Pr^iOH (for the isopropoxy-compound) to prevent *trans* esterification reactions.

The appearance and properties of the alkoxy-dithiophosphinato-complexes are similar to the alkyl analogues.

Yields were 25% (R = OPr^i) and 45% (R = OEt).

Crystal Structure Determination of [$Th(S_2PR_2)_4$], R = Me *or* C_6H_{11}.—Intensity measurements were carried out with a Syntex $P2_1$ automatic four-circle diffractometer, and corrected for absorption using a crystal form measured as before.[1] Crystal data, measurement methods, and structure solution are summarised in Table 1. Scattering factors for the neutral atoms were taken from ref. 12*a*, and anomalous scattering coefficients from ref. 12*b*. Computer programs for data reduction and structure solution were taken from ref. 13. The figures were prepared by the program ORTEP.[14]

TABLE 1

Summary of crystal data, intensity collection, structure solution, and refinement [a]

	[$Th\{S_2P(C_6H_{11})_2\}_4$]	[$Th(S_2PMe_2)_4$]
Formula	$C_{48}H_{88}P_4S_8Th$	$C_8H_{24}P_4S_8Th$
M	1 277.8	732.7
Dimensions (mm)	0.11 × 0.29 × 0.20	0.30 × 0.21 × 0.17
Crystal system	Monoclinic	Tetragonal
a(Å)	42.521(5)	} 10.521(1)
b(Å)	11.754(2)	
c(Å)	23.945(2)	11.936(1)
β(°)	100.285(8)	
U(Å^3)	11 775(3)	1 321.3(3)
Z	8	2
D_c (g cm^{-3})	1.44	1.84
D_m (g cm^{-3})	1.44	1.85
F(000)	5 232	700
Space group	$C2/c$	$P4_22_12$
Systematic absences	$hkl, h + k = 2n + 1$ $h0l, l = 2n + 1$	$h00, h = 2n + 1$ $(0k0, k = 2n + 1)$ $00l, l = 2n + 1$
μ (cm^{-1})	30.31	68.81
[(sinθ)/λ]$_{max.}$	0.52	0.56
Data collected	$+h$ $+k$ $\pm l$	$+h$ $+k$ $+l$
Unique reflections	6 800	561
Reflections <3σ	2 199	86
No. of observations/ no. of variables [b]	18.4	10.5
Structure solution	Patterson and Fourier	Fourier
Refinement	Block-diagonal least squares	Full-matrix least squares
R	0.048	0.030
R'	0.050	0.037
Goodness of fit	2.41	5.31

[a] In each case: Mo-K_α (niobium-filtered) radiation, λ 0.710 69 Å; 2θ—θ scan method; backgrounds by scan-profile interpretation (H. Blessing, P. Coppens, and P. Becker, *J. Appl. Crystallogr.*, 1972, **7**, 488; D. Schwarzenbach, 'TWOTHLEH,' a Syntex $P2_1$ data collection program including scan profile interpretation, Abstracts, Fourth European Crystallographic Meeting, Oxford, 1977, p. 134); function minimised, $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2$. [b] All $I > 3\ \sigma(I)$ reflections and those $I < 3\sigma(I)$ reflections for which $|F_c| > |F_o|$ were included in the least-squares calculation.

The structure of [$Th\{S_2P(C_6H_{11})_2\}_4$] was solved by conventional Patterson and Fourier techniques.

In [$Th(S_2PMe_2)_4$] there are only two molecules per unit cell, hence the Th atom was placed at 0,0,0 (symmetry 222) in the space group $P4_22_12$ and the rest of the structure was solved by conventional Fourier methods. The final posi-

TABLE 2

Final positional parameters for [$Th(S_2PMe_2)_4$] with estimated standard deviations in parentheses

Atom	X	Y	Z
Th	0	0	0
S(1)	−0.086 7(4)	0.240 2(4)	0.097 8(3)
S(2)	0.180 5(4)	0.093 9(4)	0.161 1(4)
P	0.079 2(4)	0.253 1(4)	0.179 2(3)
C(1)	0.173(2)	0.389(1)	0.126(1)
C(2)	0.046(1)	0.282(2)	0.331(1)

TABLE 3

Final positional parameters for [$Th\{S_2P(C_6H_{11})_2\}_4$] with estimated standard deviations in parentheses

Atom	X	Y	Z
Th	0.127 48(1)	0.124 44(4)	0.224 18(2)
P(1)	0.165 14(8)	0.149 2(3)	0.368 4(1)
S(1)	0.129 40(8)	0.248 2(3)	0.330 2(1)
S(2)	0.170 69(8)	0.017 2(3)	0.316 9(1)
P(2)	0.194 68(8)	0.205 1(3)	0.162 6(1)
S(3)	0.173 94(8)	0.302 9(3)	0.214 9(1)
S(4)	0.173 47(8)	0.052 0(3)	0.154 9(1)
P(3)	0.065 75(8)	0.283 4(3)	0.138 8(1)
S(5)	0.091 11(8)	0.158 1(3)	0.109 9(1)
S(6)	0.084 51(8)	0.317 5(3)	0.220 2(1)
P(4)	0.086 56(8)	−0.138 3(3)	0.228 6(1)
S(7)	0.123 94(8)	−0.112 0(3)	0.189 1(1)
S(8)	0.072 91(8)	0.011 1(3)	0.258 8(1)
C(1)	0.156 7(3)	0.095 1(9)	0.436 6(4)
C(2)	0.150 7(3)	0.201(1)	0.474 8(5)
C(3)	0.142 3(3)	0.150(1)	0.531 4(5)
C(4)	0.113 0(3)	0.079(1)	0.520 5(6)
C(5)	0.118 3(3)	−0.026(1)	0.483 3(6)
C(6)	0.127 4(3)	0.016(1)	0.424 1(5)
C(7)	0.202 9(3)	0.229(1)	0.378 6(6)
C(8)	0.199 9(4)	0.357(1)	0.388 7(6)
C(9)	0.233 1(4)	0.414(1)	0.389 4(7)
C(10)	0.261 0(4)	0.358(2)	0.421 5(7)
C(11)	0.263 6(4)	0.232(1)	0.413 8(6)
C(12)	0.230 6(4)	0.164(1)	0.411 1(7)
C(13)	0.238 1(3)	0.184(1)	0.187 3(5)
C(14)	0.243 0(3)	0.112(1)	0.242 5(6)
C(15)	0.279 4(4)	0.084(1)	0.260 9(6)
C(16)	0.298 6(4)	0.194(1)	0.271 8(7)
C(17)	0.294 0(5)	0.259(2)	0.217 2(8)
C(18)	0.256 5(4)	0.297(2)	0.201 2(7)
C(19)	0.187 2(3)	0.267(1)	0.089 5(5)
C(20)	0.207 2(3)	0.197(1)	0.052 2(6)
C(21)	0.195 5(4)	0.241(2)	−0.012 0(7)
C(22)	0.200 4(4)	0.368(2)	−0.015 1(7)
C(23)	0.181 4(4)	0.435(1)	0.023 8(7)
C(24)	0.193 7(3)	0.393(1)	0.087 4(6)
C(25)	0.066 6(3)	0.415 0(9)	0.096 6(5)
C(26)	0.053 2(3)	0.392(1)	0.033 5(5)
C(27)	0.054 1(4)	0.507(1)	−0.000 9(6)
C(28)	0.089 8(4)	0.549(1)	0.007 5(6)
C(29)	0.103 4(4)	0.571(1)	0.069 9(6)
C(30)	0.102 3(3)	0.454(1)	0.105 1(5)
C(31)	0.024 1(3)	0.237(1)	0.139 9(5)
C(32)	0.004 5(3)	0.339(1)	0.155 0(6)
C(33)	−0.028 8(4)	0.284(1)	0.167 0(7)
C(34)	−0.044 4(4)	0.220(2)	0.115 8(8)
C(35)	−0.024 3(4)	0.124(2)	0.097 7(7)
C(36)	0.008 1(4)	0.178(1)	0.084 8(6)
C(37)	0.102 3(3)	−0.236(1)	0.289 1(6)
C(38)	0.084 2(4)	−0.240(1)	0.333 7(7)
C(39)	0.103 4(3)	−0.312(1)	0.385 0(6)
C(40)	0.112 6(4)	−0.432(1)	0.362 4(7)
C(41)	0.128 3(4)	−0.428(1)	0.314 2(8)
C(42)	0.109 5(3)	−0.354(1)	0.262 2(6)
C(43)	0.055 3(3)	−0.206(1)	0.175 1(6)
C(44)	0.044 7(3)	−0.120(1)	0.127 7(6)
C(45)	0.019 3(4)	−0.179(1)	0.076 5(7)
C(46)	−0.007 7(4)	−0.223(2)	0.105 0(8)
C(47)	0.003 6(4)	−0.312(1)	0.150 5(7)
C(48)	0.026 8(4)	−0.251(1)	0.200 2(7)

tional parameters for all non-hydrogen atoms are reported in Tables 2 and 3. Bond lengths and angles for the complexes are given in Tables 4 and 5. Final observed and calculated structure factors along with the temperature factors are listed in Supplementary Publication No. SUP 23050 (30 pp.).†

TABLE 4

Bond lengths (Å) and angles (°) in [Th(S_2PMe_2)$_4$] with estimated standard deviations in parentheses *

(*a*) Distances

Th–S(1)	2.930(4)	P–S(2)	1.997(6)
Th–S(2)	2.878(4)	P–C(1)	1.85(2)
P–S(1)	2.003(6)	P–C(2)	1.87(1)

(*b*) Angles

S(1)–Th–S(2)	69.1(1)	S(2)–Th–S(2$^{\mathrm{III}}$)	154.1(1)
S(1)–Th–S(1$^{\mathrm{I}}$)	133.0(1)	Th–S(1)–P	88.9(2)
S(1)–Th–S(2$^{\mathrm{I}}$)	79.9(1)	Th–S(2)–P	90.5(2)
S(1)–Th–S(1$^{\mathrm{II}}$)	134.1(1)	S(1)–P–S(2)	110.9(3)
S(1)–Th–S(2$^{\mathrm{II}}$)	78.7(1)	S(1)–P–C(1)	110.5(5)
S(1)–Th–S(1$^{\mathrm{III}}$)	67.8(1)	S(1)–P–C(2)	108.7(5)
S(1)–Th–S(2$^{\mathrm{III}}$)	136.8(1)	S(2)–P–C(1)	109.0(5)
S(2)–Th–S(2$^{\mathrm{I}}$)	96.1(1)	S(2)–P–C(2)	109.9(6)
S(2)–Th–S(2$^{\mathrm{II}}$)	89.6(1)	C(1)–P–C(2)	107.7(8)

* Superscripts I—III refer to atoms generated by symmetry: I *−x*, *−y*, *z*; II *y*, *x*, *−z*; III *−y*, *−x*, *−z*. The numbering scheme is (1): A site in dodecahedron; (2): B site in dodecahedron.

TABLE 5

Bond lengths (Å) and angles (°) in [Th{$S_2P(C_6H_{11})_2$}$_4$] with standard deviations in parentheses *

(*a*) Distances

Th–S(1)	2.915(3)	P(2)–S(3)	2.015(5)
Th–S(2)	2.905(3)	P(2)–S(4)	2.007(5)
Th–S(3)	2.917(3)	P(2)–C(13)	1.85(1)
Th–S(4)	2.909(4)	P(2)–C(19)	1.87(1)
Th–S(5)	2.919(3)	P(3)–S(5)	2.019(5)
Th–S(6)	2.904(3)	P(3)–S(6)	2.011(4)
Th–S(7)	2.899(3)	P(3)–C(25)	1.85(1)
Th–S(8)	2.921(4)	P(3)–C(31)	1.86(1)
P(1)–S(1)	2.001(4)	P(4)–S(7)	2.013(5)
P(1)–S(2)	2.022(4)	P(4)–S(8)	2.023(5)
P(1)–C(1)	1.85(1)	P(4)–C(37)	1.87(1)
P(1)–C(7)	1.84(1)	P(4)–C(43)	1.85(1)

(*b*) Angles

S(1)–Th–S(2)	68.6(1)	S(3)–Th–S(5)	94.8(1)
S(1)–Th–S(3)	78.1(1)	S(3)–Th–S(6)	82.3(1)
S(1)–Th–S(4)	136.5(1)	S(3)–Th–S(7)	131.9(1)
S(1)–Th–S(5)	132.6(1)	S(3)–Th–S(8)	158.9(1)
S(1)–Th–S(6)	63.8(1)	S(4)–Th–S(5)	78.6(1)
S(1)–Th–S(7)	136.3(1)	S(4)–Th–S(6)	133.9(1)
S(1)–Th–S(8)	83.1(1)	S(4)–Th–S(7)	63.9(1)
S(2)–Th–S(3)	91.5(1)	S(4)–Th–S(8)	132.6(1)
S(2)–Th–S(4)	84.9(1)	S(5)–Th–S(6)	68.8(1)
S(2)–Th–S(5)	158.8(1)	S(5)–Th–S(7)	82.4(1)
S(2)–Th–S(6)	132.3(1)	S(5)–Th–S(8)	90.8(1)
S(2)–Th–S(7)	78.4(1)	S(6)–Th–S(7)	137.7(1)
S(2)–Th–S(8)	90.6(1)	S(6)–Th–S(8)	80.7(1)
S(3)–Th–S(4)	68.5(1)	S(7)–Th–S(8)	69.0(1)
Th–S(1)–P(1)	90.5(1)	S(3)–P(2)–C(19)	109.9(4)
Th–S(2)–P(1)	90.4(1)	S(4)–P(2)–C(13)	108.2(4)
Th–S(3)–P(2)	90.9(1)	S(4)–P(2)–C(19)	105.2(4)
Th–S(4)–P(2)	91.3(2)	C(13)–P(2)–C(19)	110.2(6)
Th–S(5)–P(3)	90.3(1)	S(5)–P(3)–S(6)	109.5(2)
Th–S(6)–P(3)	90.8(1)	S(5)–P(3)–C(25)	111.1(4)
Th–S(7)–P(4)	90.9(2)	S(5)–P(3)–C(31)	111.0(4)
Th–S(8)–P(4)	90.1(2)	S(6)–P(3)–C(25)	108.6(4)
S(1)–P(1)–S(2)	109.2(2)	S(6)–P(3)–C(31)	105.0(4)
S(1)–P(1)–C(1)	110.7(4)	C(25)–P(3)–C(31)	111.4(5)
S(1)–P(1)–C(7)	109.8(5)	S(7)–P(4)–S(8)	109.6(2)
S(2)–P(1)–C(1)	109.7(4)	S(7)–P(4)–C(37)	104.7(5)
S(2)–P(1)–C(7)	106.1(5)	S(7)–P(4)–C(43)	105.7(5)
C(1)–P(1)–C(7)	111.2(5)	S(8)–P(4)–C(37)	109.9(5)
S(3)–P(2)–S(4)	109.2(2)	S(8)–P(4)–C(43)	113.9(5)
S(3)–P(2)–C(13)	113.7(4)	C(37)–P(4)–C(43)	112.6(6)

Cyclohexyl rings: C–C 1.43(2)—1.63(2) Å, av. 1.55 Å, C–C–C 105(1)—120(1)°, av. 110°.

* The numbering scheme is 1,4,6,7: A site in dodecahedron; 2,3,5,8: B site in dodecahedron.

RESULTS AND DISCUSSION

Hydrated thorium(IV) chloride reacts rapidly with Na^+ or NH_4^+ salts of dithiophosphinic acids, R_2PS_2H, in ethanol solution to form the neutral tetrakis complexes [Th(S_2PR_2)$_4$] (R = Me, Et, Pr^i, Ph, C_6H_{11}, OEt, or OPr^i). These compounds may be extracted with CH_2Cl_2 after initial solvent removal, and recrystallized from ethanol–CH_2Cl_2 mixtures. For R = OPr^i, Pr^{i}OH was used instead of ethanol to prevent *trans* esterification.[2] All isolated complexes were analysed for Th, C, H, and S and the results (Table 6) are in good accord with the tetrakis formulation.

TABLE 6

Elemental analyses for [Th(S_2PR_2)$_4$]

	Analysis (%) *			
R	C	H	S	Th
Me	13.1	3.30	35.25	31.85
	(13.1)	(3.30)	(35.0)	(31.65)
Et	22.25	4.65	30.9	28.2
	(22.75)	(4.75)	(30.35)	(27.45)
Pr^i	28.75	5.65	25.85	25.65
	(30.1)	(5.90)	(26.8)	(24.25)
Ph	44.4	3.15	20.55	18.6
	(46.9)	(3.30)	(20.85)	(18.9)
C_6H_{11}	45.05	6.90	20.0	18.0
	(45.1)	(6.95)	(20.1)	(18.15)
OEt	19.75	4.15	26.4	24.1
	(19.75)	(4.15)	(26.35)	(23.85)
OPr^i	26.5	5.15	23.85	21.75
	(26.55)	(5.20)	(23.65)	(21.4)

* Calculated values are given in parentheses.

All of the adducts were air-stable for some weeks in contrast to the behaviour observed for the actinide(IV) dithiocarbamate analogues.[7] This confirms the observation made for the lanthanide compounds[2] that the S_2PR_2 complexes are more stable than their S_2CNR_2 analogues and hence easier to handle.

In a previous paper[2] on S_2PR_2 complexes of the lanthanides, we suggested that the nature of the product was largely determined by steric effects, a bulky ligand favouring a lower co-ordination number. Both the methyl and ethoxy-ligands gave only the tetrakis adducts with all lanthanides, whereas with the bulkier cyclohexyl ligand only La—Nd had large enough ionic radii to accommodate four such ligands. For La and Ce only the 4 : 1 adducts were formed, but reaction of Pr and Nd with 3 mol of the ligand led to the isolation of the neutral tris complexes. For the smaller lanthanoids (Sm—Lu, Y) tris complexes are formed exclusively under all conditions.

It is interesting that in the present work only the 4 : 1 stoicheiometry was observed even with the cyclohexyl

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

ligand and on lowering the metal-to-ligand reaction ratio to 1 : 3. The ionic radius of Th^{4+}, 0.984 Å,[15] lies between the values for Nd^{3+} and Pm^{3+}.[16] In other words it would be expected that both stoicheiometries should also be observed for Th with the cyclohexyl ligand on ionic radius grounds. Reasons for this disparity may lie in the higher charge density of Th^{4+}, and the possibly greater covalent Th–S interaction.

TABLE 7

Infrared band assignments cm^{-1} for $[Th(S_2PR_2)_4]$ *

R	Me	Et	Pr^i	Ph	C_6H_{11}	OEt	OPr^i
ν(M–S)	298m-s 287m-s 251s	290 (sh) 260s	270s 262s 255m-s	235m	248s	272m-s	285m
$\nu_{asym.}$(P–S)	610s 597s	618s 607 (sh)	678s 653s 639s	570s	638s	678vs 659s 644vs	676s
$\nu_{sym.}$(P–S)	509m-s	503s	503m	490m-w	573m-s 562m-s 517s	552s 547m-s	553s

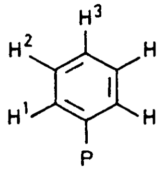
* m = Medium, s = strong, m-w = medium-weak, sh = shoulder, vs = very strong.

It is thus probable that all of the thorium complexes obtained in the present work contain the metal co-ordinated to eight sulphur atoms as demonstrated by the two structure determinations discussed below.

Infra-red Spectra.—The i.r. spectra (200—4 000 cm^{-1}) of these complexes are similar to the salts of the ligands as expected. The only noticeable differences are observed for the ν(M–S) and ν(PS_2) vibrations (below). The wavenumbers of the bands due to PS_2 and Th–S vibrations are presented in Table 7.

TABLE 8

Hydrogen-1 n.m.r. data for $[Th(S_2PR_2)_4]$

R	δ (p.p.m.)	J (Hz)
Me	1.93 (CH_3) doublet	$J_{PH} = 11.8$
Et	1.27 (CH_3) doublet of triplets 2.15 (CH_2) doublet of quartets	$J_{PH} = 21.6$ $J_{PH} = 10.0$ $\}J_{HH} = 7.4$
Pr^i	1.23 (CH_3) doublet of quartets 4.23 (CH) doublet of septets	$J_{PH} = 20.0$ $J_{PH} = 10.2$ $\}J_{HH} = 7.2$
Ph 	7.70 ($H^1 = H^5$) 7.50 (H^3) 7.35 ($H^2 = H^4$) complex multiplets, see text	$J_{PH^1} = J_{PH^5} = 15.2$ $J_{PH^2} = J_{PH^4} = 3.4$ $J_{PH^3} = 2.8$ $J_{H^1H^5} = J_{H^1H^3} = J_{H^3H^5} = 1.4$ $J_{H^1H^2} = J_{H^5H^4} = 8.3$ $J_{H^1H^4} = J_{H^2H^5} = 0.6$ $J_{H^2H^4} = 1.8$ $J_{H^2H^3} = J_{H^3H^4} = 7.6$
C_6H_{11}	1.0—2.2 complex multiplet (see text)	
OEt	1.27 (CH_3) triplet 4.11 (CH_2) doublet of quartets	J_{PH} *ca.* 0 $J_{PH} = 9.0$ $\}J_{HH} = 7.0$
OPr^i	1.26 (CH_3) doublet 4.85 (CH) doublet of septets	J_{PH} *ca.* 0 $J_{PH} = 13.0$ $\}J_{HH} = 6.2$

Bands in the 200—300 cm^{-1} region are assigned to ν(M–S) vibrations on the basis of comparisons between the spectra of ligand and complex, and by analogy with similar assignments made in this region for similar transition metal,[17] lanthanide,[2] and actinide [7] complexes. By similar comparisons, bands in the region 500—700 cm^{-1} are assigned to the $\nu_{sym.}$ and $\nu_{asym.}$ vibrations of the PS_2 unit.[2]

The absence of co-ordinated or lattice solvent in any of the compounds was confirmed by the absence of ν(O–H) and δ(O–H) vibrations in the 3 300 and 1 640 cm^{-1} regions respectively.

It is interesting to compare the M–S vibrations and P–S frequencies with those observed for the lanthanide analogues. Although the heavier Th^{4+} ion might be expected to move ν(M–S) to lower frequency, it appears that the higher charge on the metal more than compensates for this effect, so that ν(Th–S) was observed to be 10—20 cm^{-1} higher than ν(M–S) for the lanthanide analogues. It is possible that this electrostatic force may also be aided by a higher covalent contribution to the bond due to the softer nature of Th with the possibility of a contribution by the 5*f* orbitals. No consistent variation of the P–S frequencies was observed, however.

It may be significant that ν(M–S) observed for the Ph and C_6H_{11} complexes is lower than for the other ligands, perhaps indicating an increased steric interaction between ligands for the bulky Ph and C_6H_{11} substituents leading to a weaker M–S bond. This was supported by a similar observation for the lanthanide compounds [2] and by an increase in the Th–S bond length in the C_6H_{11} compound relative to the Me compound (see below).

Nuclear Magnetic Resonance Spectra.—The ^{1}H chemical shifts and coupling constants for the complexes are summarised in Table 8.

The spectra of the compounds with R = Me, Et, Pr^i, OEt, and OPr^i are first order. The 80 MHz spectrum of the phenyl compound was extremely complicated, however, many of the second-order effects were eliminated at 360 MHz. The spectrum was analysed as an AA′KK′-QQ′X system with the program PANIC [18] and all shifts and coupling constants determined.

The variation in the J_{PH} couplings is noteworthy. For the alkyl compounds $^2J_{PH}$ is smaller than $^3J_{PH}$, and similarly, for the alkoxy-compounds $^3J_{PH}$ is much greater than $^4J_{PH}$ (*ca.* 0).

Only one type of substituent at phosphorus is observed in solution in all cases, although two types may be distinguished in the solid (see below). That the alkyl resonance doublets are due to J_{PH} coupling and not to a different chemical environment of groups within the same ligand or within the co-ordination sphere was confirmed by measuring the spectra at two different field strengths. The single observed alkyl environment is due to rapid reorientation of the co-ordination polyhedron as is common for high co-ordination numbers.[8]

The spectrum of the cyclohexyl compound is interesting in that only a broad badly resolved signal was observed at 80 MHz at room temperature. However, on remeasuring the spectrum at 360 MHz, 42 well resolved lines were obtained in the region 1.11—2.22 p.p.m. At the present time the interpretation of this spectrum is incomplete. These observations are clearly due to a dynamic process which is effectively blocked at room temperature at 360 MHz, but is at the coalescence temperature at 80 MHz. Whether this is due to flipping of the cyclohexyl rings or to an unusually slow fluxional behaviour of the co-ordination polyhedron caused by large substituents cannot be determined without a complete analysis of the spectrum and its temperature dependence.

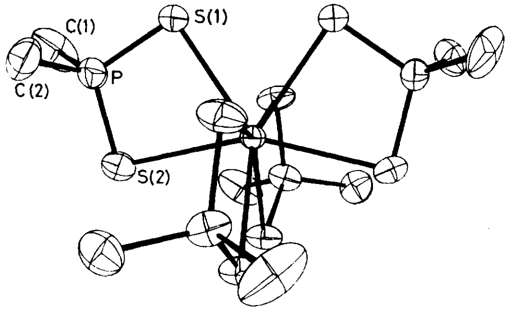


FIGURE 1 Structure of [$Th(S_2PMe_2)_4$]

The Structures of [$Th(S_2PR_2)_4$], R = Me *or* C_6H_{11}. An ORTEP [14] plot of the methyl complex is presented in Figure 1. Since the co-ordination polyhedra are almost identical only the single structure is illustrated. The co-ordination polyhedron is also shown (Figure 2).

The Th^{4+} ions are surrounded by eight sulphur atoms from the four dithiophosphinate ligands. The co-ordination polyhedra were analysed by the program POLY [19] according to the method suggested by Dollase.[20] Both were found to be almost perfect dodecahedra with the bidentate ligands occupying the *m* edges *i.e.* the *mmmm* isomer is formed.

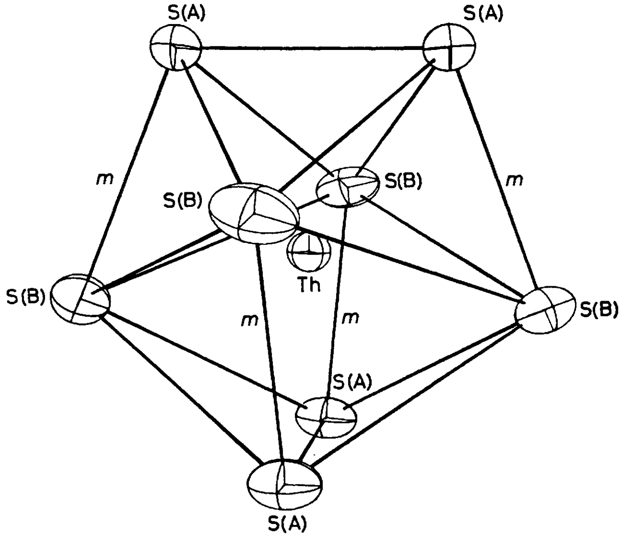


FIGURE 2 Co-ordination polyhedron of [$Th(S_2PMe_2)_4$]

The analysis gave the following values for the root-mean-square deviation (Δ) in Å of the sulphur atoms from their ideal positions: R = Me, $\Delta = 0.030$; R = C_6H_{11}, $\Delta = 0.021$.

Drew [9] has reported a range of values for structures with the *mmmm* dodecahedron which vary from 0 to 0.132 Å, hence the present structures are close to ideal. The two most common regular polyhedra for eight-co-ordination are the dodecahedron and the square antiprism. If the ligands are identical and bidentate there are a total of nine possible isomers.[21] By applying the condition that each ligand must span an identical polyhedral edge, the number of possible isomers is reduced to five. Blight and Kepert [22] have calculated the ligand–ligand repulsion energies for these as a function of *b* (defined in our case as the intraligand S–S distance divided by the Th–S bond length) and report that for $b < 1.10$ the D_{2d} (*mmmm*) dodecahedron is stable. As *b* is increased to 1.10 the D_{2d} (*mmmm*) dodecahedron and D_2 (*ssss*) square antiprism become likely, and on increasing *b* to 1.15 there is a smooth change to the D_2 (*ssss*) square antiprism. For $b > 1.20$ the D_2 (*ssss*) and D_4 (*llll*) square antiprisms become likely with the D_2 (*gggg*) dodecahedron being only slightly less probable. The values for *b* calculated in the present work are: R = Me, $b = 1.14$; R = C_6H_{11}, $b = 1.13$.

Thus, on theoretical predictions one would expect the polyhedra to tend towards the D_2 square antiprism and not the almost perfect dodecahedra which are observed. It is interesting to compare the polyhedron observed[1] in the analogous eight-co-ordinate compound $[PPh_4][Pr(S_2PMe_2)_4]$ in which the analysis[9] of the polyhedron showed it to be intermediate between the *mmmm* dodecahedron and the *ssss* square antiprism. A value for b of 1.12 was calculated[1] for the praseodymium compound, thus, the observed polyhedron agrees with the predictions of Blight and Kepert. In the present case other factors may influence the polyhedra, such as packing or bonding effects, although a few other examples of the *mmmm* dodecahedron do exist for bites of up to 1.17.[9]

The majority of the dodecahedral molecules reviewed by Drew[9] exhibited a difference in the $M-L_A$ and $M-L_B$ bond lengths for the two different co-ordination sites, A and B, in the dodecahedron, particularly for $b > 1.0$, when $M-L_A > M-L_B$. In the methyl compound, $Th-S_A$ [2.930(4) Å] is significantly longer than the $Th-S_B$ bond [2.878(4) Å], Table 4, which accords with the reported work.[9] No similar trend is observed for the cyclohexyl compound (Table 5). This may be due to the influence of the bulky C_6H_{11} groups.

It is instructive to compare the M–S bond lengths found for the present thorium compounds with those of a few analogous lanthanide, actinide, and transition-metal compounds. Table 9 lists some M–S bond lengths as well as the value remaining when the radius of the metal ion has been subtracted.

TABLE 9

Comparison of bond data for dithiophosphate and dithiocarbamate complexes

Compound	d_{M-S} (Å)	$d_{M-S} - r_{M^{n+}}$ (Å)
$[La\{S_2P(OEt)_2\}_3(OPPh_3)_2]$ [a]	3.08	2.02
$[Sm\{S_2P(OEt)_2\}_2(OPPh_3)_3]^+$ [a]	2.92	1.96
$[Pr(S_2PMe_2)_4]^-$ [a]	2.97	1.96
$[Pr\{S_2P(C_6H_{11})_2\}_3]$ [a]	2.84	1.83
$[V\{S_2P(OEt)_2\}_3]$ [a]	2.46	1.72
$[Th(S_2PMe_2)_4]$	2.90	1.92
$[Th\{S_2P(C_6H_{11})_2\}_4]$	2.91	1.93
$[Th(S_2CNEt_2)_4]$ [b]	2.87	1.89
$[Np(S_2CNEt_2)_4]^-$ [b]	2.87	1.88

[a] Values from ref. 1. [b] Values from ref. 7.

A shortening of the Th–S bond is observed which cannot be explained only on the basis of the ionic radii, which is less for $[Th(S_2PMe_2)_4]$ than for the analogous praseodymium, samarium, or lanthanum compounds. This supports a stronger M–S interaction for the Th case and correlates with the i.r. ν(M–S) observations. As mentioned earlier, this is probably due to the higher charge density on Th and perhaps a stronger covalent interaction.

For the cyclohexyl compound, $d_{M-S} - r_{M^{n+}}$ is slightly greater than for the methyl compound which may be due to the increased interligand interactions of the cyclohexyl substituents. In both cases the M–S bond is longer than for the S_2CNR_2 complexes due to the smaller S_2CNR_2 bite.

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