

## Synthesis of Thorium(IV)thiophosphinates. Structure of $[\text{Th}(\text{Ph}_2\text{P}(\text{S})\text{O})_4(\text{EtOH})_4](\text{CH}_2\text{Cl}_2)_2$

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Received June 1, 1985

### Abstract

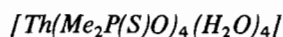
Reaction of thiophosphinate salts with  $\text{Th}^{4+}$  salts yields the complexes  $[\text{Th}(\text{R}_2\text{P}(\text{S})\text{O})_4(\text{SM})_4]$  where  $\text{R} = \text{Me}, \text{Ph}$  and  $\text{SM}$  (solvent molecule) =  $\text{H}_2\text{O}$  or  $\text{EtOH}$ . The compounds have been characterized by elemental analyses, IR, Raman and mass spectra. According to the spectra and to a crystal structure determination of the title compound (tetragonal, space group  $P\bar{4}2_1c$ , with  $a = 1784.0(7)$ ,  $c = 1045.8(4)$  pm,  $R = 0.024$ ) the  $\text{R}_2\text{P}(\text{S})\text{O}$ -ligands are coordinated to thorium by their O-atoms only. Four solvent molecules complete the dodecahedral coordination sphere. The Th–O (ligand) bond distance of 229.1(3) pm is unexpectedly small.

### Introduction

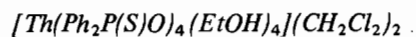
Recently several alkyl- and aryl-dithiophosphinate ( $\text{R}_2\text{PS}_2^-$ ) and -thiophosphinate ( $\text{R}_2\text{P}(\text{S})\text{O}^-$ ) complexes of lanthanides have been prepared and structurally characterized. In these compounds the dithiophosphinates generally behave as bidentate ligands, leading to monomeric complexes [1]. The corresponding thiophosphinates usually act as monodentate O-donor ligands, and only in a few cases as bidentate O,S-donors [2]. They prefer also polymeric structures because of their anisobidentate character [3]. Pinkerton and coworkers have recently described the dodecahedral dithiophosphinate complexes  $\text{Th}(\text{S}_2\text{PR}_2)_4$  [1]. These authors suggest that  $\text{Th}^{4+}$  has a 'softer' character than the  $\text{Ln}^{3+}$ -ions, and that the 5f orbitals of thorium are more easily accessible for bonding than the 4f orbitals of the lanthanides. To elucidate further the behaviour of S-donor ligands towards the actinides, we extended our work on thiophosphinate complexes [4] to thorium(IV).  $\text{Th}^{4+}$  may be coordinated by these ligands monodentate through oxygen or bidentate through oxygen and sulfur, but polymeric structures cannot be ruled out.

### Experimental

#### Synthesis



A solution of 2.85 g (0.005 mol)  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  in ethanol is slowly added to an ethanolic solution of 3.18 g (0.02 mol)  $\text{Na}[\text{Me}_2\text{P}(\text{S})\text{O}] \cdot 1.5\text{H}_2\text{O}$  [5] at 50 °C. A white suspension is formed which is evaporated to dryness *in vacuo* and extracted with  $\text{CH}_2\text{Cl}_2$ . Recrystallization from  $\text{CH}_2\text{Cl}_2$ . Yield 25%. *Anal.* Found: C, 12.9; H, 4.06; Th, 32.0. Calc.: C, 12.97; H, 4.32; Th, 31.4%.



Anhydrous  $\text{Th}(\text{NO}_3)_4$  was prepared by refluxing a solution of 2.85 g (0.005 mol)  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  in methyl cyanide for 20 h through a Soxhlet-extractor packed with molecular sieves [6]. 5.46 g (0.02 mol) Kalium-diphenylthiophosphinat (from  $\text{Ph}_2\text{P}(\text{S})\text{OH}$  [7] and  $\text{KOH}$  in ethanol) are added and again refluxed for 5 h in the Soxhlet. The solution is then concentrated to 100 ml. The precipitate is filtered off and recrystallized several times from  $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$  (10:1). *Anal.* Found: C, 46.5; H, 4.05. Calc. for  $\text{C}_{58}\text{H}_{68}\text{Cl}_4\text{O}_8\text{P}_4\text{S}_4\text{Th}$ : C, 45.8; H, 4.50%.

#### Crystal Data and Structure Determination

Unit cell: tetragonal,  $a = 1784.0(7)$ ,  $c = 1045.8(4)$  pm,  $V = 3328.4 \times 10^6$  pm<sup>3</sup>, space group  $P\bar{4}2_1c$ ,  $D_x = 1.51$  g cm<sup>-3</sup>. A crystal with the dimensions  $0.2 \times 0.1 \times 0.1$  mm was used for data collection at 140 K on a Syntex P2<sub>1</sub> four-circle diffractometer, equipped with a graphite monochromator. 4111 reflections, up to  $2\theta = 54^\circ$  were measured employing  $\text{Mo K}\alpha$  radiation and the  $\theta/2\theta$  scan technique with variable scan speeds 3.9–29.3° min<sup>-1</sup>. After averaging of symmetry-related data 2048 reflections remained, of which 1807 with  $I \geq 1.96\sigma(I)$  were considered observed. The difficult structure was solved by careful interpretation of a Patterson map, where sites for the Th-, S-, P- and coordinated O-atoms could be found ( $R = 0.167$ ). The remaining nonhydrogen

TABLE I. Fractional Coordinates and Thermal Parameters

Atom	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$B_{\text{eq}}^a$ ( $B_{\text{iso}}$ )
Th	0000.0	0000.0	0000.0	1.33(6)
S	1724.5(8)	1086.5(8)	2681.9(15)	2.84(6)
P	1913.5(7)	0293.5(7)	1414.3(13)	1.87(5)
O1	1218(2)	0011(3)	0694(3)	1.99(11)
O2	0047(2)	0821(2)	1993(3)	2.12(13)
C1	2577(3)	0604(3)	0224(5)	2.99(24)
C2	2969(3)	1275(4)	0390(6)	3.41(27)
C3	3522(5)	1504(5)	4492(9)	2.15(41)
C4	3930(6)	1369(4)	3455(9)	5.40(45)
C5	4595(6)	1758(5)	3256(8)	5.27(44)
C6	4828(4)	2301(4)	4155(6)	4.03(32)
C7	2678(3)	4462(3)	2869(5)	2.06(20)
C8	2730(3)	3774(3)	35077(6)	3.06(26)
C9	2411(4)	3133(4)	2995(7)	3.84(31)
C10	2051(4)	3175(4)	1846(8)	4.01(36)
C11	1990(4)	3847(4)	1192(7)	4.47(34)
C12	3211(4)	4492(4)	1717(6)	3.36(28)
C13A	4512(8)	3861(9)	2205(15)	4.41(3)
C13B	4632(7)	4239(7)	1774(11)	2.77(2)
C14A	4849(8)	3476(8)	1030(13)	4.07(3)
C14B	4453(10)	3451(10)	1292(17)	5.26(4)
C15	0000.0	5000	4696(10)	5.67(55)
Cl	0705(1)	4599(1)	3753(2)	5.48(10)
Atom	$x \times 10^3$	$y \times 10^3$	$z \times 10^3$	$B$
H2	291(4)	167(4)	136(7)	6.5(21)
H3	299(4)	133(5)	454(7)	5.7(20)
H4	380(4)	091(4)	276(7)	7.4(22)
H5	-010(4)	326(4)	235(6)	4.9(18)
H6	030(4)	233(4)	112(6)	4.8(17)
H8	293(4)	369(4)	434(6)	4.6(16)
H10	196(4)	275(4)	156(7)	4.7(18)
H11	173(3)	385(3)	038(5)	3.0(13)
H12	233(4)	491(4)	126(6)	4.7(16)

$$^a B_{\text{eq}} = (B_{11}B_{22}B_{33})^{1/3}.$$

atoms of the complex, a solvent molecule and all but one hydrogen atom at the phenyl groups were localized in subsequent difference Fourier maps. The carbon atoms of the ethanol molecules proved to be disordered over two sites. They have been included in the refinement as split atoms. Several cycles of full-matrix least-squares refinement (weighting scheme  $w^{-1} = \sigma(F_o)^2 + (0.01 F_o)^2$ ) of 214 variables, with anisotropic thermal factors for all nonhydrogen atoms except the C (ethanol) atoms, converged to  $R = 0.024$  ( $R_w = 0.027$ ). For all computations the program system E-XTL was used. Table I contains the final fractional coordinates.

## Results and Discussion

$\text{Na}^+$  or  $\text{K}^+$  salts of thiophosphinic acids  $\text{R}_2\text{P}(\text{S})\text{OH}$  ( $\text{R} = \text{Ph}, \text{Me}$ ) react in ethanol solution with  $\text{Th}^{4+}$  to

form the neutral complexes  $[\text{Th}(\text{R}_2\text{P}(\text{S})\text{O})_4(\text{SM})_4]$  ( $\text{SM} = \text{solvent molecules like } \text{H}_2\text{O} \text{ or } \text{C}_2\text{H}_5\text{OH}$ ). They can be extracted with  $\text{CH}_2\text{Cl}_2$ . Their IR and Raman spectra differ from the spectra of alkali metal thiophosphinates in two significant points: the broad  $\nu\text{PO}$  absorption is shifted from  $1080 \text{ cm}^{-1}$  to  $1020 \text{ cm}^{-1}$  and  $\nu\text{PS}$  (intense in the Raman spectra) from  $545$  to  $570 \text{ cm}^{-1}$ . These shifts clearly indicate that the ligands are coordinated through their oxygen atoms only. The remaining free coordination sites at the central atom in the probably eight coordinated complexes are occupied by donor atoms of the solvent molecules. Similar observations have been made for the thiophosphinate complexes of the lanthanides [2]. The solvent molecules are split off below  $160^\circ\text{C}$  according to DTA measurements on  $[\text{Th}(\text{Me}_2\text{P}(\text{S})\text{O})_4(\text{H}_2\text{O})_4]$ . Its mass spectrum ( $222^\circ\text{C}$ ,  $70 \text{ eV}$ ) contained an intense peak at  $m/e = 668 \text{ u}$  due to  $[\text{Th}(\text{Me}_2\text{P}(\text{S})\text{O})_4]^+$ .

### Structure of $[\text{Th}(\text{Ph}_2\text{P}(\text{S})\text{O})_4(\text{EtOH})_4]$

The complex molecule is situated on a special position of the unit cell with the point symmetry  $\bar{4}$ . The thorium atom is surrounded by the oxygen atoms of 4 thiophosphinate ligands (O1) and by the oxygen atoms of 4 ethanol molecules (O2) (see Fig. 1). These 8 oxygen atoms form a distorted dodecahedron with O1 at the B and O2 at the A coordination sites of the dodecahedron [7]. The Th—O distances differ remarkably (see Table II). Th—O1,  $229.1(3) \text{ pm}$ , is to our knowledge the shortest Th—O distance observed so far in a  $\text{Th}^{4+}$ -complex with eightfold coordination. The bonding interaction is very probably mainly ionic. But it is difficult to rationalize its strength. The P—O bond is also rather short. Their length is certainly in the double bond region. If one compares the M—O (ligand) bond lengths in the present thorium compound and in similar lanthanide compounds — regarding their different ionic radii —, the Th—O and the Ln—O

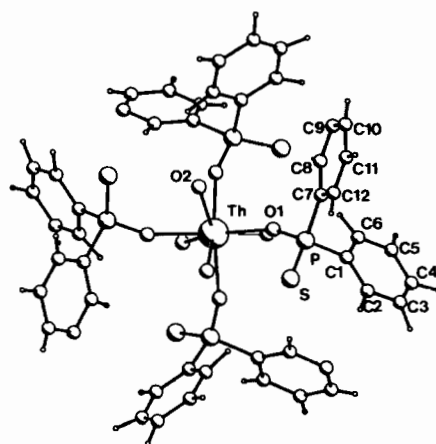


Fig. 1. ORTEP-Plot of  $\text{Th}(\text{Ph}_2\text{P}(\text{S})\text{O})_4(\text{EtOH})_4$  (only O-atoms of EtOH are shown for clarity).

TABLE II. Important Bond Lengths (pm) and Bond Angles (deg)

Th-O1	229.1(3)
Th-O2	254.9(3)
P-O1	153.7(3)
S...O2	311.5(4)
P-S	196.8(2)
P-C1	180.5(6)
P-C7	181.4(5)
O2...O2	293.4(5)
Th-O1-P	157.5(2)
S-P-O1	115.3(2)
S-P-C1	110.9(2)
S-P-C7	112.2(2)
O1-P-C1	106.9(2)
O1-Th-O1'	95.8(1)
O1-Th-O1''	143.1(1)
O1-Th-O2	72.8(1)
O1-Th-O2'	143.5(1)
Th-O2-C13A	134.8(7)
Th-O2-C13B	130.5(5)
O1-P-C7	105.0(2)
C1-P-C7	105.8(2)
O1-Th-O2''	77.1(1)
O1-Th-O2'''	73.4(1)
O2-Th-O2'	132.0(1)
O2-Th-O2''	70.3(1)
P-S...O2	84.2(1)

bonds have the same relative lengths. Contrary to the lanthanides [2], S-coordinated thiophosphinate complexes of thorium are unknown. Therefore a 'softer' character cannot be assigned to thorium, at least in the present case.

The sulfur atom in the P-S-bond is acceptor of a rather strong hydrogen bond of 311.5(4) pm length. The bond originates from the OH group of the

coordinated ethanol molecules. The P-S...O2 angle is close to 90°. One can assume therefore, that a p $\pi$ -orbital of sulfur is involved in the hydrogen bond. Similar observations have been made in the related lanthanide compounds [2] and in the solid state structure of thiophosphinic acids [8, 9]. The Th-OC<sub>2</sub>H<sub>5</sub> bonds are rather weak. The carbon atoms of the ethanol molecules are disordered over two positions, which are referred by a rotation of 46° around the Th-O2 bond. The reason for the disorder is not completely clear. Pure sterical reasons and the possibility of the OH-group to form also a hydrogen bond to a neighbouring O2 atom at the distance 293.4(5) pm can be discussed. The occupancy of the position, from which the O...S hydrogen bond (*vide supra*) can be formed, seems to be slightly preferred. The CH<sub>2</sub>Cl<sub>2</sub> molecules are placed on the twofold axes in holes of the structure.

## References

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