*SHELX*76 (Sheldrick, 1976) using scattering factors of Cromer & Mann (1968).

Discussion. Atomic positions and equivalent isotropic thermal parameters are given in Table 1,* bond lengths and angles in Table 2. Fig. 1 shows the environment of the Cu atom; Fig. 2 is a perspective view of the unit cell. The coordination polyhedron is a square pyramid formed by two monodentate carboxylic groups of different acid molecules and three water molecules, the base of the pyramid being slightly distorted towards a tetrahedron. An analogous coordination sphere was observed in copper(II) 1,2,4,5-benzenetetracarboxylate decahydrate (Usubaliev, Shnulin & Mamedov, 1982). As two of the carboxyl groups act as ligands, polymeric zigzag chains are formed, which run along **b**. These are connected into sheets *via* hydrogen bonding: O(5)—H(4)···O(2^{i}) [O(5)···O(2^{i}) = 2·566 Å]. Intermolecular distances O(7)···O(4^{ii}) = 2·705 Å and O(8)···O(4^{ii}) = 2·690 Å indicate hydrogen bonding between neighbouring sheets. [Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.]

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44844 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Biagini Cingi, M., Manotti Lanfredi, A. M., Tiripicchio, A. & Tiripicchio Camellini, M. (1981). *Acta Cryst.* B**37**, 2159–2163.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Prout, C. K., Carruthers, J. R. & Rossotti, F. J. C. (1971). *J. Chem. Soc. A*, pp. 3350–3354.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Usubaliev, B. T., Shnulin, A. N. & Mamedov, Kh. S. (1982). *Koord. Khim.* **8**(11), 1532–1538.

Acta Cryst. (1988). C**44**, 994–996

Structure of Tetrachlorotris(triphenylphosphine oxide)thorium(IV)

By G. Van den Bossche

Cristallographie B5, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

J. Rebizant

Commission of the European Communities, JRC Karlsruhe, Postfach 2266, D-7500 Karlsruhe,
Federal Republic of Germany

M. R. Spirlet

Physique Expérimentale B5, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

and J. Goffart*

Institut de Radiochimie B16, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

(*Received* 26 *October* 1987; *accepted* 29 *January* 1988)

Abstract. $[ThCl_4\{OP(C_6H_5)_3\}_3]$, $M_r = 1208{\cdot}73$, triclinic, $P\bar{1}$, $a = 10{\cdot}668\ (7)$, $b = 13{\cdot}857\ (7)$, $c = 20{\cdot}141\ (6)$ Å, $\alpha = 98{\cdot}23\ (4)$, $\beta = 77{\cdot}98\ (4)$, $\gamma = 100{\cdot}67\ (8)°$, $V = 2845\ (5)$ Å^3, $Z = 2$, $D_x = 1{\cdot}411$ g cm^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 30{\cdot}212$ cm^{-1}, $F(000) = 1192$, $T = 295\ (1)$ K, $R = 0{\cdot}052$ for 4671 observed reflections with $I > 3\sigma(I)$. The Th atom is seven-coordinate in an approximate capped-octahedral environment with an O in the capping position and three Cl atoms in the capped face. The packing in the crystal is dictated by van der Waals interactions.

Introduction. Numerous substituted tertiary phosphine oxide complexes of thorium and uranium tetrahalides are now known but very few structural data are available for complexes of the type ThX_4L_3 (X = Cl or Br; L = oxygen-donor ligand). The structure analysis of the title compound has been undertaken with the aim of clarifying the stoichiometric and conformational changes induced by relatively bulky oxygen-donor ligands.

---

* Chercheur Qualifié FNRS.

0108-2701/88/060994-03$03.00

Experimental. Addition of triphenylphosphine to a solution of thorium tetrachloride in tetrahydrofuran and crystallization at 283 K yielded single crystals of the title complex. Crystal 0·25 × 0·20 × 0·15 mm. Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\bar{\alpha}$ radiation. Cell parameters refined by least squares from angle data of 25 reflections in range 12–24° (2θ). 9189 reflections collected (θ–2θ scan mode) in range $3 \leq 2\theta \leq 52°$, h −7/7, k −9/9, l −13/13; 7397 reflections considered observed [$I \geq \sigma(I)$], averaged to 5681 unique reflections ($R_{\rm int} = 0{\cdot}02$), 4671 reflections with $I > 3\sigma(I)$ used in refinement. Three reflections monitored periodically showed no significant deviations from mean. Intensities corrected for Lorentz–polarization effects; empirical absorption corrections (transmission factors range from 88·73 to 99·93%). Structure solved by direct methods and Fourier techniques; full-matrix least-squares refinement {minimizing $\sum w(\Delta F)^2$; $w = 1/[\sigma(F_o)]^2$ with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma^2(I) + (AI)^2]^{1/2}/{\rm Lp}$ where A, the ignorance factor, is 0·07}. Anisotropic thermal parameters for Th, Cl, O and P atoms; isotropic for C atoms; H atoms in calculated positions, included in final structure-factor calculation with $B_{\rm iso} = 5{\cdot}0$ Å^2. A secondary-extinction coefficient refined to $g = 2{\cdot}1 \times 10^{-7}$ {$F_c = F_c/[1 + g(F_c)^2{\rm Lp}]$}. $R = 0{\cdot}052$, $wR = 0{\cdot}084$, $S = 1{\cdot}934$, $(\Delta/\sigma)_{\rm max} = 0{\cdot}01$, $\Delta\rho$ in final difference Fourier map within 1·043 and −0·785 e Å^{-3}. Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1981) *SDP* programs.

Discussion. The structure consists of discrete molecules of [ThCl$_4$(OPPh$_3$)$_3$] which are illustrated in Fig. 1 together with the atomic number scheme. Final atomic coordinates for non-H atoms are given in Table 1;* selected interatomic distances, angles and short intramolecular contacts are reported in Table 2.

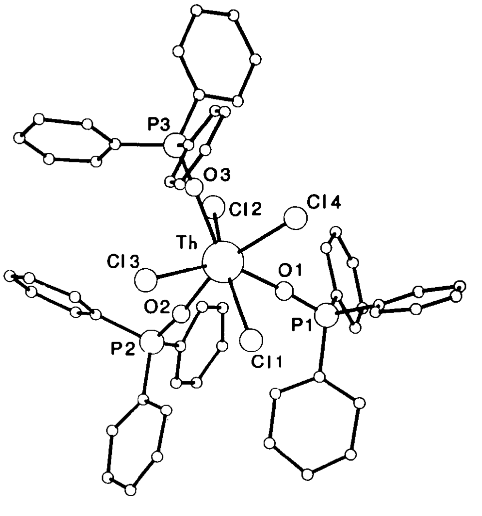

Fig. 1. The molecular structure of the title compound with atom numbering.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (*e.s.d.'s in parentheses*)

	x	y	z	$B_{\rm eq}$*/$B_{\rm iso}$(Å^2)
Th	0·14656 (6)	0·20703 (5)	0·23409 (3)	2·53 (1)
Cl(1)	−0·0409 (4)	0·1278 (3)	0·3346 (2)	4·7 (1)
Cl(2)	0·3983 (4)	0·2593 (4)	0·1695 (2)	4·9 (1)
Cl(3)	−0·0266 (4)	0·0985 (3)	0·1586 (2)	4·7 (1)
Cl(4)	0·0880 (5)	0·3854 (4)	0·2986 (3)	5·8 (1)
O(1)	0·257 (1)	0·2183 (8)	0·3256 (5)	4·0 (3)
O(2)	0·2177 (9)	0·0516 (7)	0·2133 (5)	3·6 (3)
O(3)	0·141 (1)	0·3049 (8)	0·1456 (5)	4·0 (3)
P(1)	0·2966 (4)	0·2238 (3)	0·3935 (2)	3·6 (1)
P(2)	0·2744 (4)	−0·0439 (3)	0·1928 (2)	3·4 (1)
P(3)	0·1189 (4)	0·3597 (3)	0·0944 (2)	3·4 (1)
C(1)	0·245 (2)	0·109 (1)	0·4308 (8)	4·0 (4)
C(2)	0·219 (2)	0·116 (2)	0·501 (1)	8·1 (6)
C(3)	0·178 (3)	0·017 (2)	0·528 (1)	10·1 (8)
C(4)	0·170 (2)	−0·073 (2)	0·488 (1)	8·3 (6)
C(5)	0·196 (2)	−0·068 (2)	0·417 (1)	9·4 (7)
C(6)	0·237 (2)	0·024 (2)	0·388 (1)	8·0 (6)
C(7)	0·227 (2)	0·318 (1)	0·4563 (8)	4·0 (4)
C(8)	0·096 (2)	0·318 (1)	0·4640 (9)	4·5 (4)
C(9)	0·034 (2)	0·383 (2)	0·516 (1)	7·1 (5)
C(10)	0·108 (2)	0·446 (2)	0·553 (1)	7·4 (6)
C(11)	0·241 (2)	0·450 (2)	0·544 (1)	9·0 (7)
C(12)	0·301 (2)	0·381 (2)	0·493 (1)	6·6 (5)
C(13)	0·470 (1)	0·249 (1)	0·3837 (8)	3·7 (3)
C(14)	0·529 (2)	0·207 (2)	0·426 (1)	6·4 (5)
C(15)	0·676 (2)	0·232 (2)	0·413 (1)	8·5 (7)
C(16)	0·742 (2)	0·291 (2)	0·366 (1)	6·6 (5)
C(17)	0·678 (2)	0·333 (2)	0·327 (1)	6·4 (5)
C(18)	0·538 (2)	0·311 (1)	0·3335 (9)	5·0 (4)
C(19)	0·305 (1)	−0·070 (1)	0·1009 (8)	3·7 (3)
C(20)	0·418 (2)	−0·107 (1)	0·0675 (9)	5·1 (4)
C(21)	0·432 (2)	−0·129 (2)	−0·004 (1)	6·3 (5)
C(22)	0·338 (2)	−0·116 (1)	−0·037 (1)	6·0 (5)
C(23)	0·230 (2)	−0·081 (1)	−0·005 (1)	5·9 (5)
C(24)	0·211 (2)	−0·053 (1)	0·0671 (9)	4·9 (4)
C(25)	0·162 (1)	−0·146 (1)	0·2289 (8)	3·4 (3)
C(26)	0·187 (2)	−0·246 (1)	0·210 (1)	5·6 (5)
C(27)	0·098 (2)	−0·325 (2)	0·242 (1)	6·4 (5)
C(28)	−0·013 (2)	−0·303 (2)	0·285 (1)	7·6 (6)
C(29)	−0·048 (2)	−0·204 (2)	0·298 (1)	8·6 (7)
C(30)	0·046 (2)	−0·121 (1)	0·272 (1)	6·1 (5)
C(31)	0·424 (2)	−0·035 (1)	0·2233 (8)	4·0 (4)
C(32)	0·507 (2)	0·053 (1)	0·2189 (9)	4·6 (4)
C(33)	0·626 (2)	0·061 (1)	0·239 (1)	5·8 (5)
C(34)	0·662 (2)	−0·013 (2)	0·263 (1)	6·6 (5)
C(35)	0·588 (2)	−0·104 (2)	0·261 (1)	9·3 (7)
C(36)	0·461 (2)	−0·114 (2)	0·242 (1)	8·5 (7)
C(37)	−0·035 (1)	0·397 (1)	0·1188 (8)	3·4 (3)
C(38)	−0·051 (2)	0·495 (1)	0·130 (1)	5·7 (5)
C(39)	−0·186 (2)	0·523 (2)	0·150 (1)	7·3 (6)
C(40)	−0·293 (2)	0·444 (2)	0·158 (1)	6·6 (5)
C(41)	−0·271 (2)	0·347 (2)	0·148 (1)	6·2 (5)
C(42)	−0·140 (2)	0·322 (1)	0·127 (1)	5·5 (4)
C(43)	0·123 (1)	0·284 (1)	0·0159 (8)	3·3 (3)
C(44)	0·205 (2)	0·218 (1)	−0·0003 (9)	5·1 (4)
C(45)	0·215 (2)	0·161 (2)	−0·063 (1)	7·4 (6)
C(46)	0·143 (2)	0·170 (2)	−0·111 (1)	6·6 (5)
C(47)	0·058 (2)	0·241 (2)	−0·095 (1)	6·6 (5)
C(48)	0·046 (2)	0·295 (1)	−0·0291 (9)	5·2 (4)
C(49)	0·242 (1)	0·464 (1)	0·0825 (8)	3·7 (3)
C(50)	0·318 (2)	0·491 (1)	0·1316 (9)	5·2 (4)
C(51)	0·425 (2)	0·575 (2)	0·119 (1)	6·6 (5)
C(52)	0·441 (2)	0·624 (2)	0·060 (2)	6·9 (5)
C(53)	0·363 (2)	0·597 (2)	0·014 (1)	7·7 (6)
C(54)	0·263 (2)	0·514 (1)	0·024 (1)	6·0 (5)

* $B_{\rm eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)]$.

---

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, C—C bond lengths and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44738 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Th environment			
Th—Cl(1)	2·728 (3)	Cl(1)—Th—Cl(2)	154·0 (1)
Th—Cl(2)	2·743 (3)	Cl(1)—Th—Cl(3)	79·3 (1)
Th—Cl(3)	2·734 (3)	Cl(1)—Th—Cl(4)	85·1 (1)
Th—Cl(4)	2·739 (4)	Cl(2)—Th—Cl(3)	118·3 (1)
Th—O(1)	2·357 (7)	Cl(2)—Th—Cl(4)	101·5 (1)
Th—O(2)	2·367 (7)	Cl(3)—Th—Cl(4)	116·6 (1)
Th—O(3)	2·404 (8)	O(1)—Th—O(2)	79·7 (3)
O(1)—Th—O(3)	137·9 (3)	Cl(2)—Th—O(3)	72·9 (2)
O(2)—Th—O(3)	123·9 (3)	Cl(3)—Th—O(1)	148·3 (2)
Cl(1)—Th—O(1)	76·7 (2)	Cl(3)—Th—O(2)	78·3 (2)
Cl(1)—Th—O(2)	86·4 (2)	Cl(3)—Th—O(3)	73·8 (2)
Cl(1)—Th—O(3)	132·7 (2)	Cl(4)—Th—O(1)	81·8 (2)
Cl(2)—Th—O(1)	79·4 (2)	Cl(4)—Th—O(2)	161·0 (2)
Cl(2)—Th—O(2)	79·4 (2)	Cl(4)—Th—O(3)	73·7 (2)
Triphenylphosphine oxide			
P(1)—O(1)	1·504 (8)	P(2)—C(25)	1·81 (1)
P(1)—C(1)	1·80 (1)	P(2)—C(31)	1·81 (1)
P(1)—C(7)	1·82 (1)	P(3)—O(3)	1·446 (8)
P(1)—C(13)	1·80 (1)	P(3)—C(37)	1·76 (1)
P(2)—O(2)	1·524 (8)	P(3)—C(43)	1·77 (1)
P(2)—C(19)	1·81 (1)	P(3)—C(49)	1·77 (1)
Th—O(1)—P(1)	167·0 (5)	C(19)—P(2)—C(25)	108·9 (6)
O(1)—P(1)—C(1)	112·1 (6)	C(19)—P(2)—C(31)	109·1 (6)
O(1)—P(1)—C(7)	112·7 (5)	C(25)—P(2)—C(31)	107·7 (6)
O(1)—P(1)—C(13)	110·2 (5)	Th—O(3)—P(3)	172·1 (5)
C(1)—P(1)—C(7)	106·0 (6)	O(3)—P(3)—C(37)	110·3 (5)
C(1)—P(1)—C(13)	106·6 (6)	O(3)—P(3)—C(43)	109·5 (5)
C(7)—P(1)—C(13)	109·0 (6)	O(3)—P(3)—C(49)	110·2 (5)
Th—O(2)—P(2)	173·4 (5)	C(37)—P(3)—C(43)	108·4 (6)
O(2)—P(2)—C(19)	109·6 (5)	C(37)—P(3)—C(49)	110·0 (6)
O(2)—P(2)—C(25)	110·4 (5)	C(43)—P(3)—C(49)	108·5 (6)
O(2)—P(2)—C(31)	111·1 (5)		
Intramolecular nonbonding contacts			
O(3)···Cl(2)	3·070 (8)		
O(3)···Cl(3)	3·095 (9)		
O(3)···Cl(4)	3·095 (9)		

The Th atom is seven-coordinate, being bonded to four chlorines and three oxygens making up the rare MX_4L_3 (X, L = unidentate ligand) stoichiometry. For many molecules of this type, repulsions between the ligands are the major factor in the choice of geometry; molecules containing halogens have geometries in which these atoms occupy the least crowded sites of the polyhedra. Thus, molecules with four halogens are capped octahedra with one halogen in the capping position and the three others in the uncapped face (Drew, 1977; Drew & Willey, 1984). Here, the geometry of the coordination approximates most nearly to a capped octahedron but with an O in the capping position [O(3)] and three chlorines in the capped face [Cl(2), Cl(3), Cl(4)].

The Th—Cl and Th—O distances are close to the average Th—Cl_{eq} and Th—O distances observed in other phosphine oxide complexes of seven-coordinate Th with pentagonal bipyramidal geometry: $ThCl_4(depa)_3$ (depa = *N*,*N*-diethylpropionamide) (Bombieri, Benetollo, Croatto, Castellani, Bagnall & Li Xing-Fu, 1984), Th—Cl_{eq} 2·754 (3), Th—Cl_{ax} 2·692 (3), Th—O 2·340 (9) Å; $ThCl_4(PhMeNCONPhMe)_3$ (Al-Daher, Bagnall, Benetollo, Polo & Bombieri, 1986), Th—Cl_{eq} 2·743 (3), Th—Cl_{ax} 2·696 (3), Th—O 2·392 (5) Å. On the other hand the Th—Cl distances are significantly greater than those reported for $ThCl_4(NMe_3)_3$ (Drew & Willey, 1984) in which the metal atom is seven-coordinate in a capped-octahedral environment with one Cl in the capping position 2·678 (10) Å and the three other Cl atoms occupying the uncapped face at 2·642 (9), 2·637 (12) and 2·685 (11) Å. This lengthening can probably be ascribed to steric factors (the presence of bulky ligands) as indicated by the close contacts of O(3) with the adjacent Cl atoms.

The P atoms show tetrahedral coordination, being surrounded by three C and one O atoms. The tetrahedral angles vary from 106·0 (6) to 112·7 (5)°. The P(3)—O(3) bond length is significantly shorter than P(1)—O(1) and P(2)—O(2) which are close to values reported for $UCl_4(OPPh_3)_2$ (Bombieri, Brown & Graziani, 1975), $U(NCS)_4(OPPh_3)_4$ (Bombieri, De Paoli, Forsellini & Brown, 1979), $UBr_4(OPPh_3)_2$ (Bombieri, Benetollo, Bagnall, Plews & Brown, 1983) and $U(cp)Cl_3(OPPh_3)_2$.thf (cp = η^5-cyclopentadienyl and thf = tetrahydrofuran) (Bagnall, Benetollo, Bombieri & De Paoli, 1984). The P—O bond length is 1·46 (1) Å in free $OPPh_3$ (Bandoli, Bortolozzo, Clemente, Croatto & Panattoni, 1970) and corresponds to the value for a strong double bond. Obviously P(3)—O(3) is a bond of this type when P(1)—O(1) and P(2)—O(2) are slightly affected and present a large degree of π character. The angles between the phenyl rings [C(1)—C(6), ring 1; C(7)—C(12), ring 2; C(13)—C(18), ring 3; C(19)—C(24), ring 4; C(25)—C(30), ring 5; C(31)—C(36), ring 6; C(37)—C(42), ring 7; C(43)—C(48), ring 8 and C(49)—C(54), ring 9] are: 1–2, 98 (2); 1–3, 84 (2); 2–3, 95 (2); 4–5, 97 (2); 4–6, 88 (2); 5–6, 55 (2); 7–8, 73 (2); 7–9, 75 (2) and 8–9, 84 (2)°. The packing in the crystal shows only van der Waals interactions.

References

Al-Daher, A. G. M., Bagnall, K. W., Benetollo, F., Polo, A. & Bombieri, G. (1986). *J. Less-Common Met.* **122**, 167–173.

Bagnall, K. W., Benetollo, F., Bombieri, G. & De Paoli, G. (1984). *J. Chem. Soc. Dalton Trans.* pp. 67–73.

Bandoli, G., Bortolozzo, G., Clemente, D. A., Croatto, U. & Panattoni, C. (1970). *J. Chem. Soc. A*, pp. 2778–2780.

Bombieri, G., Benetollo, F., Bagnall, K. W., Plews, M. J. & Brown, D. (1983). *J. Chem. Soc. Dalton Trans.* pp. 343–348.

Bombieri, G., Benetollo, F., Croatto, U., Castellani, C. B., Bagnall, K. W. & Li Xing-Fu (1984). *Inorg. Chim. Acta*, **95**, 237–245.

Bombieri, G., Brown, D. & Graziani, R. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1873–1876.

Bombieri, G., De Paoli, G., Forsellini, E. & Brown, D. (1979). *J. Inorg. Nucl. Chem.* **41**, 1315–1320.

Drew, M. G. B. (1977). *Prog. Inorg. Chem.* **23**, 67–210.

Drew, M. G. B. & Willey, G. R. (1984). *J. Chem. Soc. Dalton Trans.* pp. 727–729.

Enraf–Nonius (1981). *Structure Determination Package*, version 18. Enraf–Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)