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The Crystal Structure of Tetranitratobis(triphenylphosphine oxide)thorium(IV)

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The crystal structure has been determined from three-dimensional X-ray data collected by photographic methods. The crystals are monoclinic, with unit-cell dimensions $a=14{\cdot}081$ (5), $b=17{\cdot}590$ (5), $c=16{\cdot}567$ (5) Å, $\beta=91{\cdot}02$ (10)°; the space group is $P2_1/n$ and $Z=4$. The structure was solved by Patterson and Fourier methods, and refined by the least-squares method on the basis of 3933 independent observations. The final value of conventional R is 0·1009. The thorium atom has a coordination number of ten involving eight oxygen atoms from four bidentate nitrate groups and two oxygen atoms from the Th–O–P linkages as immediate neighbours. The triphenylphosphine groups are linked with thorium through Th–O–P linkages and are related by an approximate twofold axis of symmetry passing through the thorium atom. The phosphorus atoms have irregular tetrahedral coordination with average P–C bond length = 1·80 (3) and P–O = 1·45 (2) Å. The phenyl rings are planar with average C–C distance = 1·40 (6) Å. The Th–O(bridging) distances, 2·37 (2) and 2·33 (2) Å, are shorter than the Th–O(nitrate) distances, 2·52 (2) to 2·58 (2) Å. The nitrate groups are planar with average N–O distance = 1·24 (6) Å.

Introduction

Lea (1968) and Mackay made preliminary X-ray investigations of tetranitratobis(triphenylphosphine oxide)thorium(IV), and collected intensity data out to $\theta=20°$ for Mo $K\alpha$ radiation on a 4-circle diffractometer as a development project. Although the approximate position of the thorium atom and some indications of the rest of the structure were correctly obtained from these data, refinement could not be achieved and comparison of $|F_o|$ and $|F_c|$ showed that there must be gross errors in the data, probably due to movement of the crystal in its mount leading to incorrect setting and possibly incorrect indexing in some cases. The existence of these errors was subsequently confirmed when photographic data were obtained. It is of interest that so much information could be extracted from data with $(\sin\theta)/\lambda<0{\cdot}5$, part of which was grossly in error. However, since the extent of the errors was unknown at the time, the structure determination was started again without reference to the previous work.

Experimental

A single crystal shaped to a sphere (diameter, 0·214 mm) and mounted about the a axis was obtained from Dr A. L. Mackay. The crystal was grown by Smith & Wassef (1968).

Crystal data

Tetranitratobis(triphenylphosphine oxide)thorium(IV), $Th(NO_3)_4[(C_6H_5)_3PO]_2$, F.W. 1036·6. Monoclinic, $a=14{\cdot}081$ (5), $b=17{\cdot}590$ (5), $c=16{\cdot}567$ (5) Å, $\beta=91{\cdot}02$ (10)°; space group, $P2_1/n$. $V=4103$ Å^3; $D_m=1{\cdot}655$ g cm^{-3}; $D_c=1{\cdot}679$ g cm^{-3}; $Z=4$; $F(000)=2024$; linear absorption coefficient = 164·2 cm^{-1} ($\lambda=1{\cdot}542$ Å).

The crystal data given above are those obtained by Lea (1968). With the exception of D_m, they were all redetermined in the present work and agreement obtained within the limits of error.

The intensities ($0kl$–$7kl$) were collected on non-integrating Weissenberg photographs with the multiple film technique and Cu $K\alpha$ radiation. The intensities were estimated visually. Approximate spot-shape corrections were applied on the low-angle, upper-level reflexions by multiplying the observed intensity of a particular spot by the ratio of its length to that of the spot on the intensity scale. The film correlation factors were determined by using a program based on the method of Hamilton, Rollett & Sparks (1965). The raw intensities were corrected for Lorentz, polarization and absorption effects to give 3933 unique reflexions including about 500 'unobserveds' (given a value of half the minimum observable intensity).

Structure determination

The Th atom was located from a three-dimensional Patterson synthesis. A three-dimensional density map computed with the Th phases revealed the Th–O–P linkages. A second electron density map computed with the phases obtained from the Th and P positions and weighted $|F_o|$ values revealed all the 57 non-hydrogen atoms in the structure. The weights were calculated from the relation, $w=\tanh(2|F_o|\,|F_c|/\sum_i n_i f_i^2)$, where n_i is the number of atoms with scattering power f_i in the unit cell not included in $|F_c|$.

The structure was refined by the method of least squares. The quantity minimized was $\sum w(|F_o|-G|F_c|)^2$. The weights were calculated from the relation, $w=1/(60+|F_o|+0{\cdot}0055|F_o|^2)$ and gave reasonably constant averages of $w\Delta F^2$ with $|F_o|$ and $(\sin\theta)/\lambda$ at the end of refinement. In a given cycle of refinement, the positional and thermal parameters of only a selected number of atoms and the eight scale factors were varied, the rest of the structure being treated as 'fixed' atom contributors. The refinement, with Th and P atoms anisotropic and including full corrections for anomalous dispersion ($\Delta f'$ and $\Delta f''$) for these two atom types (*International Tables for X-ray Crystallography*, 1962),

Table 1. *Fractional co-ordinates with e.s.d.'s* ($\times 10^5$) *of all the non-hydrogen atoms in one molecule*

	x	y	z
Th	0·02110 (8)	0·15563 (4)	0·19739 (4)
P(1)	0·28209 (62)	0·18498 (36)	0·24856 (33)
P(2)	−0·22615 (59)	0·10142 (32)	0·26290 (35)
O(1)	0·18668 (176)	0·16829 (91)	0·22281 (104)
O(2)	−0·13351 (147)	0·12097 (84)	0·22868 (91)
N(1)	−0·04023 (248)	0·27200 (140)	0·08153 (159)
O(11)	−0·04794 (190)	0·32501 (129)	0·03303 (137)
O(12)	−0·09171 (163)	0·24947 (103)	0·12954 (114)
O(13)	0·05032 (166)	0·24819 (90)	0·08276 (93)
N(2)	0·05457 (215)	0·08819 (105)	0·04358 (128)
O(21)	0·05210 (152)	0·06314 (99)	−0·02731 (105)
O(22)	0·11826 (163)	0·08772 (94)	0·08929 (109)
O(23)	−0·03719 (164)	0·09763 (85)	0·06569 (93)
N(3)	0·02189 (204)	0·28113 (123)	0·30827 (135)
O(31)	0·02623 (228)	0·33507 (144)	0·36330 (168)
O(32)	−0·01042 (154)	0·21969 (101)	0·33254 (111)
O(33)	0·05004 (166)	0·29406 (107)	0·24351 (123)
N(4)	0·04425 (180)	0·00864 (116)	0·28548 (124)
O(41)	0·04904 (196)	−0·05276 (141)	0·31878 (147)
O(42)	0·05696 (137)	0·06946 (87)	0·31925 (91)
O(43)	0·02565 (136)	0·01279 (93)	0·21126 (97)
C(111)	0·33026 (203)	0·09422 (120)	0·28452 (131)
C(112)	0·31425 (237)	0·02977 (146)	0·24430 (157)
C(113)	0·35257 (309)	−0·03544 (206)	0·26830 (228)
C(114)	0·41303 (331)	−0·03336 (227)	0·34279 (255)
C(115)	0·43597 (269)	0·03544 (178)	0·37794 (184)
C(116)	0·39443 (222)	0·10134 (136)	0·34716 (149)
C(121)	0·28361 (183)	0·25343 (104)	0·32636 (114)
C(122)	0·33239 (248)	0·32132 (158)	0·31632 (166)
C(123)	0·33386 (242)	0·37557 (156)	0·37668 (168)
C(124)	0·28889 (260)	0·36163 (163)	0·45070 (177)
C(125)	0·23479 (271)	0·29468 (178)	0·46119 (184)
C(126)	0·23222 (242)	0·24106 (158)	0·39813 (170)
C(131)	0·34933 (273)	0·21179 (137)	0·16200 (154)
C(132)	0·44914 (369)	0·22323 (199)	0·17049 (227)
C(133)	0·50692 (399)	0·24387 (276)	0·10544 (341)
C(134)	0·45236 (453)	0·25193 (240)	0·03328 (274)
C(135)	0·36524 (401)	0·25529 (204)	0·01903 (225)
C(136)	0·30360 (302)	0·23394 (206)	0·08904 (228)
C(211)	−0·29466 (236)	0·18464 (151)	0·29012 (159)
C(212)	−0·28352 (229)	0·23938 (152)	0·23743 (155)
C(213)	−0·32869 (295)	0·31475 (196)	0·25166 (211)
C(214)	−0·38740 (226)	0·31835 (136)	0·32170 (151)
C(215)	−0·39698 (201)	0·26206 (120)	0·37283 (128)
C(216)	−0·36357 (286)	0·19472 (203)	0·35969 (205)
C(221)	−0·21552 (205)	0·04455 (118)	0·34962 (127)
C(222)	−0·27838 (234)	−0·02167 (150)	0·36195 (162)
C(223)	−0·25788 (333)	−0·06491 (225)	0·43461 (249)
C(224)	−0·19215 (323)	−0·03534 (209)	0·48852 (231)
C(225)	−0·13751 (292)	0·03183 (186)	0·47870 (198)
C(226)	−0·14971 (237)	0·06713 (148)	0·40610 (161)
C(231)	−0·29810 (297)	0·04812 (142)	0·19038 (150)
C(232)	−0·39210 (426)	0·05299 (238)	0·18657 (245)
C(233)	−0·43646 (343)	0·01301 (239)	0·12628 (261)
C(234)	−0·38661 (314)	−0·04074 (157)	0·07425 (176)
C(235)	−0·28524 (319)	−0·03750 (157)	0·07430 (179)
C(236)	−0·23684 (225)	0·00268 (139)	0·13487 (152)

Table 2. *Thermal parameters* ($\times 10^3$), *anisotropic for* Th *and* P *atoms and isotropic for all other non-hydrogen atoms*

E.s.d.'s are given in parentheses. The anisotropic temperature factor has the form,

$$T=\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2klb^*c^*U_{23}+2lhc^*a^*U_{31})\right].$$

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{21}$
Th	66 (1)	68 (1)	65 (1)	−1 (1)	13 (1)	1 (1)
P(1)	68 (9)	92 (4)	62 (3)	−6 (5)	−3 (7)	−8 (8)
P(2)	59 (8)	79 (3)	78 (4)	−3 (5)	8 (7)	−19 (7)

	U_{iso}		U_{iso}		U_{iso}
O(1)	97 (5)	C(111)	79 (6)	C(211)	99 (8)
O(2)	85 (4)	C(112)	98 (8)	C(212)	100 (8)
N(1)	114 (8)	C(113)	145 (13)	C(213)	134 (11)
O(11)	135 (7)	C(114)	159 (14)	C(214)	90 (7)
O(12)	109 (6)	C(115)	121 (10)	C(215)	78 (6)
O(13)	92 (5)	C(116)	92 (7)	C(216)	134 (11)
N(2)	89 (6)	C(121)	66 (5)	C(221)	77 (6)
O(21)	104 (5)	C(122)	105 (8)	C(222)	102 (8)
O(22)	102 (5)	C(123)	106 (8)	C(223)	157 (14)
O(23)	91 (5)	C(124)	109 (9)	C(224)	145 (13)
N(3)	99 (6)	C(125)	121 (9)	C(225)	130 (11)
O(31)	164 (9)	C(126)	108 (8)	C(226)	101 (8)
O(32)	108 (6)	C(131)	95 (8)	C(231)	96 (8)
O(33)	116 (6)	C(132)	142 (12)	C(232)	162 (15)
N(4)	92 (6)	C(133)	194 (18)	C(233)	164 (15)
O(41)	150 (8)	C(134)	168 (16)	C(234)	111 (9)
O(42)	89 (5)	C(135)	141 (13)	C(235)	113 (9)
O(43)	94 (5)	C(136)	145 (13)	C(236)	93 (7)

Table 3. *Calculated positions of the hydrogen atoms in the phenyl rings*

The H atom is given the same number as that of its parent carbon atom. Assumed C–H distance = 1·084 Å.

	x	y	z
H(112)	0·269	0·031	0·191
H(113)	0·340	−0·088	0·235
H(114)	0·439	−0·086	0·369
H(115)	0·486	0·038	0·429
H(116)	0·412	0·157	0·372
H(122)	0·370	0·332	0·261
H(123)	0·370	0·429	0·367
H(124)	0·296	0·402	0·450
H(125)	0·196	0·285	0·516
H(126)	0·191	0·190	0·404
H(132)	0·482	0·216	0·230
H(133)	0·583	0·252	0·110
H(134)	0·495	0·256	−0·020
H(135)	0·336	0·272	−0·039
H(136)	0·227	0·236	0·084
H(212)	−0·242	0·230	0·184
H(213)	−0·318	0·363	0·212
H(214)	−0·426	0·371	0·333
H(215)	−0·434	0·272	0·428
H(216)	−0·384	0·147	0·397
H(222)	−0·335	−0·037	0·320
H(223)	−0·293	−0·119	0·446
H(224)	−0·181	−0·067	0·544
H(225)	−0·090	0·053	0·526
H(226)	−0·105	0·116	0·393
H(232)	−0·432	0·087	0·229
H(233)	−0·512	0·215	0·116
H(234)	−0·425	−0·081	0·037
H(235)	−0·246	−0·066	0·027
H(236)	−0·160	0·001	0·141

converged at a conventional *R* value of 0·1006. Average parameter shift/e.s.d. = 0·01. The positions of the thirty hydrogen atoms belonging to the six phenyl rings were calculated based on a C–H distance of 1·084 Å (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1958). These atoms were given temperature factors equal to their parent carbon atoms and included in the final structure factor calculations (*R* = 0·1009), but no attempt was made to refine them. The atomic scattering factors for all the atoms were those given by Hanson, Herman, Lea & Skillman (1964). The positional and thermal parameters of all the non-hydrogen atoms are given in Tables 1 and 2 respectively.* The calculated H atom positions are listed in Table 3. The computations were made with the *HRS*, *LP*, *FOURIER*, *SFLS* and *MOLGOM* programs of Birkbeck College Crystallographic Program Library on the University of London CDC 6600 computer.

Description and discussion of the structure

The crystal structure of tetranitratobis(triphenylphosphine oxide)Th(IV) consists of discrete molecular units having the chemical formula, $Th(NO_3)_4[(C_6H_5)_3PO]_2$. The molecular structure of this compound is shown in Fig. 1. The important interatomic distances and angles with their e.s.d.'s are listed in Table 4.

Coordination of Th(IV)

The thorium atom has a coordination number of ten involving eight oxygen atoms from four bidentate nitrate groups and two oxygen atoms from two Th–O–P linkages. The variations in Th–O(nitrate) bond distances, 2·52 (2) to 2·58 (2) Å [average distance = 2·55 (2) Å] are probably not significant. The Th–O (bridging) distances, 2·37 (2) Å and 2·33 (2) Å [average = 2·35 (2) Å] are not significantly different but undoubtedly differ from the Th–O (nitrate) distances. This accords with the general expectation that the Th–O (bridging) distances should be less than the Th–O (nitrate) distances because the oxygen atom in the Th–O–P linkage is much more tightly bound than that in a nitrate group.

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* A list of structure factors has been deposited with the National Lending Library, England, as supplementary Publication No. SUP 30163 (34 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Interatomic distances and angles, uncorrected for thermal motion*

E.s.d.'s are given in parentheses, (× 10^2) for distances and (× 1) for angles.

Bond lengths involving Th	
Th–O(1)	2·37 (2) Å
Th–O(2)	2·33 (2)
Mean Th–O (bridging)	2·35 (2)
Th–O(12)	2·54 (2)
Th–O(13)	2·54 (2)
Th–O(22)	2·57 (2)
Th–O(23)	2·53 (2)
Th–O(32)	2·55 (2)
Th–O(33)	2·58 (2)
Th–O(42)	2·57 (2)
Th–O(43)	2·52 (2)
Mean Th–O (nitrate)	2·55 (2)
Bond lengths involving P atoms	
P(1)–O(1)	1·43 (2) Å
P(2)–O(2)	1·47 (2)
Mean P–O	1·45 (2)
P(1)–C(111)	1·83 (2)
P(1)–C(121)	1·76 (2)
P(1)–C(131)	1·80 (3)
P(2)–C(211)	1·81 (3)
P(2)–C(221)	1·75 (2)
P(2)–C(231)	1·82 (3)
Mean P–C	1·80 (3) Å

Nitrate groups	
N(1)–O(11)	1·23 (3)
N(1)–O(12)	1·17 (3)
N(1)–O(13)	1·34 (3)
N(2)–O(21)	1·25 (2)
N(2)–O(22)	1·17 (3)
N(2)–O(23)	1·35 (3)
N(3)–O(31)	1·32 (3)
N(3)–O(32)	1·25 (3)
N(3)–O(33)	1·17 (3)
N(4)–O(41)	1·21 (3)
N(4)–O(42)	1·22 (2)
N(4)–O(43)	1·25 (2)
Mean N–O	1·24 (6)
O(11)···O(12)	2·18 (3)
O(11)···O(13)	2·09 (3)
O(12)···O(13)	2·16 (3)
O(21)···O(22)	2·17 (3)
O(21)···O(23)	2·10 (3)
O(22)···O(23)	2·22 (3)
O(31)···O(32)	2·15 (3)
O(31)···O(33)	2·14 (3)
O(32)···O(33)	2·16 (3)
O(41)···O(42)	2·15 (3)
O(41)···O(43)	2·14 (3)
O(42)···O(43)	2·09 (2)
Mean O···O	2·15

Phenyl rings	
C(111)–C(112)	1·33 (3) Å
C(112)–C(113)	1·33 (4)
C(113)–C(114)	1·49 (5)
C(114)–C(115)	1·38 (4)
C(115)–C(116)	1·39 (4)
C(116)–C(111)	1·37 (3)
C(121)–C(122)	1·39 (3)
C(122)–C(123)	1·38 (4)
C(123)–C(124)	1·41 (4)
C(124)–C(125)	1·41 (4)
C(125)–C(126)	1·41 (4)
C(126)–C(121)	1·42 (3)
C(131)–C(132)	1·42 (4)
C(132)–C(133)	1·41 (6)
C(133)–C(134)	1·42 (6)
C(134)–C(135)	1·25 (5)
C(135)–C(136)	1·51 (5)
C(136)–C(131)	1·41 (4)
C(211)–C(212)	1·31 (3)
C(212)–C(213)	1·49 (4)
C(213)–C(214)	1·42 (4)
C(214)–C(215)	1·31 (3)
C(215)–C(216)	1·29 (4)
C(216)–C(211)	1·53 (4)
C(221)–C(222)	1·48 (3)
C(222)–C(223)	1·45 (4)
C(223)–C(224)	1·38 (5)
C(224)–C(225)	1·42 (4)
C(225)–C(226)	1·36 (4)
C(226)–C(221)	1·36 (3)
C(231)–C(232)	1·33 (5)
C(232)–C(233)	1·36 (5)
C(233)–C(234)	1·47 (5)
C(234)–C(235)	1·43 (4)
C(235)–C(236)	1·39 (4)
C(236)–C(231)	1·50 (4)
Mean C–C	1·40 (6)

Table 4 (*cont.*)

Important bond angles	
Th—O(1)–P(1)	170·2 (1·1)°
Th—O(1)–P(2)	170·2 (1·0)
O(1)—P(1)–C(111)	105·0 (0·4)
O(1)—P(1)–C(121)	110·9 (0·9)
O(1)—P(1)–C(131)	108·7 (1·2)
O(2)—P(2)–C(211)	112·7 (0·3)
O(2)—P(2)–C(221)	112·6 (0·5)
O(2)—P(2)–C(231)	110·7 (1·2)
C(111)–P(1)–C(121)	111·0 (0·7)
C(111)–P(1)–C(131)	106·9 (1·0)
C(121)–P(1)–C(131)	113·9 (1·1)
C(211)–P(2)–C(221)	107·1 (0·3)
C(211)–P(2)–C(231)	106·7 (1·2)
C(221)–P(2)–C(231)	106·6 (0·8)
O(1)—Th–O(2)	154·8 (0·4)
O(12)–Th–O(13)	50·3 (0·5)
O(22)–Th–O(23)	51·7 (0·7)
O(32)–Th–O(33)	49·7 (0·6)
O(42)–Th–O(43)	48·4 (0·5)
O(11)–N(1)–O(12)	131·1 (3·3)
O(11)–N(1)–O(13)	108·6 (2·7)
O(12)–N(1)–O(13)	119·3 (2·2)
O(21)–N(2)–O(22)	126·9 (2·6)
O(21)–N(2)–O(23)	107·4 (2·2)
O(23)–N(2)–O(23)	123·7 (1·8)
O(31)–N(3)–O(32)	114·6 (2·2)
O(31)–N(3)–O(33)	118·8 (2·2)
O(32)–N(3)–O(33)	126·6 (1·8)
O(41)–N(4)–O(42)	124·4 (2·2)
O(41)–N(4)–O(43)	120·4 (2·1)
O(42)–N(4)–O(43)	115·2 (1·6)
P(1)–C(111)–C(112)	121·4 (1·5)
P(1)–C(111)–C(116)	113·7 (1·3)
P(1)–C(121)–C(122)	119·9 (1·8)
P(1)–C(121)–C(126)	120·5 (1·3)
P(1)–C(131)–C(132)	119·5 (2·4)
P(1)–C(131)–C(136)	121·1 (2·4)
P(2)–C(211)–C(212)	110·9 (1·9)
P(2)–C(211)–C(216)	128·9 (2·2)
P(2)–C(221)–C(222)	121·3 (1·9)
P(2)–C(221)–C(226)	116·3 (1·9)
P(2)–C(231)–C(232)	122·8 (1·9)
P(2)–C(231)–C(236)	111·1 (2·7)
C(112)–C(111)–C(116)	124·1 (1·7)°
C(111)–C(112)–C(113)	121·5 (2·8)
C(112)–C(113)–C(114)	116·8 (2·9)
C(113)–C(114)–C(115)	119·9 (3·2)
C(114)–C(115)–C(116)	118·9 (2·6)
C(115)–C(116)–C(111)	118·0 (2·2)
C(122)–C(121)–C(126)	119·5 (1·8)
C(121)–C(122)–C(123)	120·5 (2·5)
C(122)–C(123)–C(124)	120·5 (2·4)
C(123)–C(124)–C(125)	120·1 (2·4)
C(124)–C(125)–C(126)	118·2 (2·7)
C(125)–C(126)–C(121)	119·5 (1·8)
C(132)–C(131)–C(136)	118·6 (2·6)
C(131)–C(132)–C(133)	122·9 (3·8)
C(132)–C(133)–C(134)	111·1 (4·4)
C(133)–C(134)–C(135)	132·9 (4·6)
C(134)–C(135)–C(136)	114·9 (3·4)
C(135)–C(136)–C(131)	117·8 (3·6)
C(212)–C(211)–C(216)	120·1 (2·4)
C(211)–C(212)–C(213)	119·4 (2·5)
C(212)–C(213)–C(214)	114·8 (2·5)
C(213)–C(214)–C(215)	123·7 (2·3)
C(214)–C(215)–C(216)	122·7 (2·2)
C(215)–C(216)–C(211)	118·0 (2·5)
C(222)–C(221)–C(226)	122·4 (1·9)
C(221)–C(222)–C(223)	114·7 (2·0)
C(222)–C(223)–C(224)	117·6 (3·4)
C(223)–C(224)–C(225)	126·8 (3·2)
C(224)–C(225)–C(226)	114·8 (3·1)
C(225)–C(226)–C(221)	123·1 (2·1)
C(232)–C(231)–C(236)	126·0 (2·6)
C(231)–C(232)–C(233)	116·4 (3·3)
C(232)–C(233)–C(234)	123·0 (3·8)
C(233)–C(234)–C(235)	117·6 (2·5)
C(234)–C(235)–C(236)	119·7 (2·7)
C(235)–C(236)–C(231)	115·6 (2·1)

There is a pseudo-twofold axis of symmetry passing through the thorium atom and approximately parallel to the *z* axis. The oxygen atoms, O(1) and O(2), which act as bridges to link the two $-P(C_6H_5)_3$ groups with Th (in *trans* positions) lie slightly above the thorium *z* level. The distribution of the nitrate groups around thorium is more or less symmetrical in a band perpendicular to the Th–O(2) bond direction.

For coordination involving oxygen atoms one normally expects about eight neighbours of the thorium atom. But higher coordination numbers of Th(IV) have been reported in some compounds. Thus in $Th(NO_3)_4$ $5H_2O$ Ueki, Zalkin & Templeton (1966) found that thorium has three oxygen atoms from three water molecules and eight oxygen atoms from four nitrate ions as neighbours in a highly polar arrangement. Šćavničar and Prodić (1965) showed that in $Mg(H_2O)_6.Th(NO_3)_6.2H_2O$ the thorium atom is surrounded by twelve oxygen atoms from six nitrate ions. Both the above workers explained the coordination numbers of Th(IV) on the basis of the fact that the distance (~2·1 Å) between the two oxygen atoms of a particular nitrate group bonded to Th is considerably less than the sum of their atomic radii. In the magnesium complex, the gathering of the nitrate ions around Th(IV) and water molecules around Mg(II) was attributed to the greater ionic potential of Th(IV) as compared with the ionic potential of Mg(II).

The packing of ten oxygen atoms around thorium in $Th(NO_3)_4[(C_6H_5)_3PO]_2$ may be understood by a similar reasoning. The average distance along the edges of nitrate triangles (O···O = 2·15 Å) is less than the sum of their ionic radii, 2·8 Å (Pauling, 1960*a*). This gives at least a partial explanation for the occurrence of a high coordination number, ten, of Th(IV). The large cation size and vacant 5*f* electronic configuration of

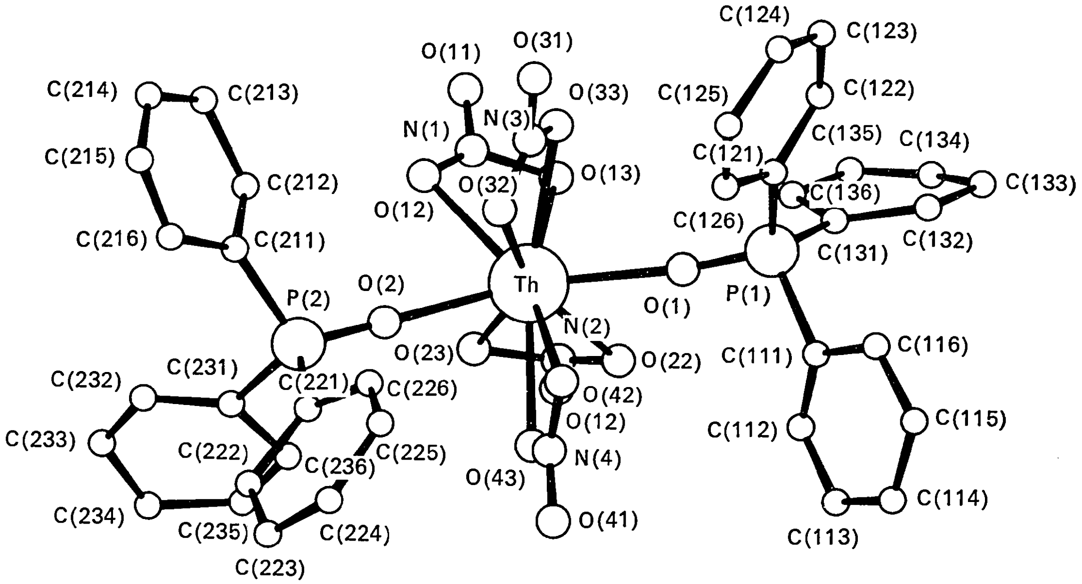

Fig. 1. $Th(NO_3)_4[(C_6H_5)_3PO]_2$ molecule viewed down **c**. For clarity H atoms are not shown.

Th(IV) are considered to be additional factors favouring a ten-coordinated structure (Muetterties, 1966).

The coordination around thorium is very difficult to describe in terms of any ideal polyhedron. If, however, one considers a nitrate group to behave as a single 'ligand site', then the coordination polyhedron may be described in terms of a slightly distorted octahedron whose two corners (*trans*) are occupied by two bridging oxygen atoms and four corners by four nitrate 'sites'. Fig. 2 is drawn to show such a distorted octahedral arrangement. For each nitrate group, the midpoint of the two oxygen atoms bonded to Th has been taken as the effective site of the ligand.

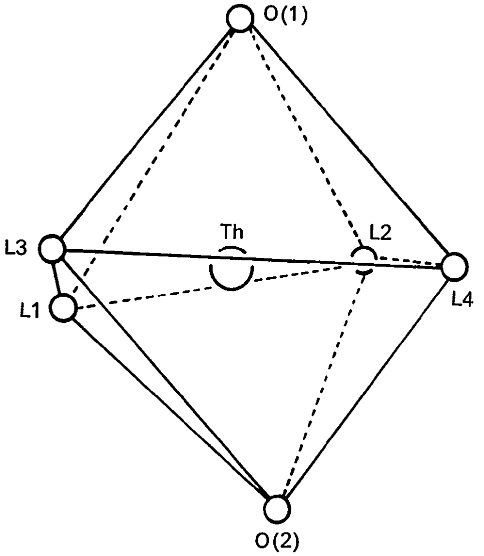

Fig. 2. Coordination polyhedron around Th considered as an irregular octahedron. O(1) and O(2) are two bridging oxygen atoms; L1, L2, L3 and L4 represent the effective sites of four nitrate groups. View along **c** axis.

The nitrate groups

All the nitrate groups are planar within experimental error (average deviation of the atoms from the least-squares planes = 0·017 Å) and as is often found (Addison, Logan, Wallwork & Garner, 1971) show slight deviations from perfect $\bar{6}2m$ symmetry.

The N–O distances vary from 1·17 (3) to 1·35 (3) Å. The average distance (1·24 Å) is comparable with N–O distances found in other nitrate complexes of Th(IV) (Ueki, Zalkin & Templeton, 1965; Taylor, Mueller & Hitterman, 1966; Šćavničar & Prodić, 1965). No systematic discrimination could be made between the N–O (next to Th) and the terminal N–O bonds. The lengths along the edges of nitrate triangles vary from 2·09 (2) to 2·22 (3) Å (average O···O = 2·15 Å). Sums of the three O–N–O angles in the nitrate groups are 359·0, 357·0, 359·0 and 360·0°.

Coordination around P *atoms*

Each of the two phosphorus atoms shows an irregular tetrahedral coordination. Three carbon atoms of three phenyl rings and the oxygen atom of the Th–O–P linkage occupy the four corners of the tetrahedron, the P atom sitting at the centre. The tetrahedral angles vary from 105·0 to 113·9°, the average being 109·4°. The deviations from the ideal tetrahedral angles may be due to the mutual repulsion of the bulky phenyl groups.

The two P–O distances are 1·43 (2) and 1·47 (2) Å. The average P–O distance, 1·45 (2) Å, is much less than the sum of the single-bond radii (1·76 Å, Pauling, 1960*b*). This shortening of the P–O bond suggests that

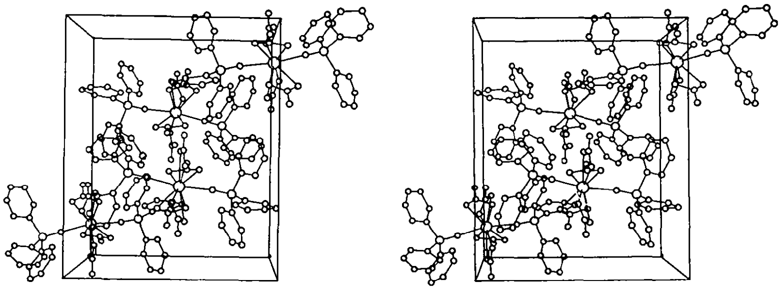

Fig. 3. Stereoscopic illustration of the contents of the unit cell. The view is down **c**, with **a** horizontal and **b** vertical.

some $d\pi$–$p\pi$ bonding may be involved owing to the tendency of the filled $p\pi$ orbitals of oxygen to overlap with empty $d\pi$ orbitals of phosphorus (Cotton & Wilkinson, 1966).

The bond lengths between phosphorus and carbon atoms of the phenyl rings range from 1·75 (2) to 1·83 (2) Å, the average P–C distance being 1·80 (3) Å. These values are close to the P–C_6H_5 distances, 1·80 (1) to 1·84 (2) Å, reported for $CH_3CCo(CO)_8P(C_6H_5)_3$ (Brice, Penfold, Robinson & Taylor, 1970) and 1·83 (1) to 1·84 (1) Å for $(C_3H_5)_2Ru[P(C_6H_5)_3]_2$ (Smith, 1972).

The phenyl (C_6H_5) *rings*

In the six phenyl rings, the average C–C bond length is 1·40 (6) Å and the average C–C–C angle is 119·8°. All the phenyl rings are planar within experimental error with an average deviation of the atoms from the least-squares plane = 0·039 Å.

The ring systems are distorted from the ideal hexagonal symmetry (6/*mmm*) of the benzene nuclei with large anomalies in some of the phenyl bond lengths and angles. This suggests considerable errors associated with a few carbon atoms which are probably due to some systematic errors in the data, inaccuracies in thorium scattering factor curve or use of limited data. The relatively small contribution by an individual carbon atom to the scattering power of the whole structure in the presence of a heavy atom like thorium makes it difficult to find the exact positions of the carbon atoms. Small errors might have also been introduced by neglecting the effect of thermal vibrations on the interatomic distances.

Molecular packing

A stereoscopic view of the packing of $Th(NO_3)_4[(C_6H_5)_3PO]_2$ molecules is shown in Fig. 3. It was found, by calculating the intermolecular contact distances, that the molecules are held together in the crystal by van der Waals forces.

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Note added in proof: – When it was too late to make any changes in the above, our attention was drawn to the structure determination of the isostructural cerium compound by Mazhar-ul-Haque, Caughlan, Hart & Van Nice (1971).

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