

Structure of Bis(4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-onato-*O,O'*)dinitratobis(triphenylphosphine oxide-*O*)thorium(IV)

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Abstract. [Th(C₁₇H₁₃N₂O₂)₂(NO₃)₂(C₁₈H₁₅OP)₂], *M_r* = 1467, orthorhombic, *Pcan*, *a* = 11.619 (10), *b* = 23.721 (10), *c* = 25.243 (4) Å, *V* = 6957.33 Å³, *Z* = 4, *D_x* = 1.40 g cm⁻³, λ(Mo *Kα*) = 0.71069 Å, μ = 23.2 cm⁻¹, *F*(000) = 2936, *T* = 298 K, *R* = 0.058 for 2547 reflections with *I* ≥ 2σ(*I*). The crystal is composed of discrete molecules containing a thorium ion coordinated to ten O atoms from two bidentate benzoyl pyrazolone anions, two bidentate nitrate anions, and two triphenylphosphine oxide molecules.

Introduction. The extraction of tetravalent actinide ions from nitric acid solutions into organic solutions of 1,3-diketones (*HA*) and neutral synergists (*L*) such as phosphine oxides has been shown to involve nitrate complexes with the general formulation *MA*_{4-*x*}(NO₃)_{*x*}*L*_{*y*} (Ramakrishna & Patil, 1984). Mixed complexes have been proposed for extraction of Pu^{IV} from nitric acid using the 1,3-diketone HBMPP (4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one) and tributylphosphate (Chmutova, Pribylova & Myasoedov, 1974). Relatively little structural information has been gathered on complexes of this type. We report here on the crystal structure of such a complex with Th^{IV}.

Experimental. Th(NO₃)₄·4H₂O (2 mmol) and HBMPP (8 mmol) were dissolved in 40 ml hot ethanol. After stirring for 1.5 h, triphenylphosphine oxide (6 mmol) was added and the clear solution stirred for several hours. The volatiles were removed at reduced pressure. Addition of a mixture of chloroform (10 ml) and heptane (20 ml) gave an oily phase which was separated from the solution by decantation and solidified under vacuum. This solid was dissolved in ethanol (25 ml) and 7 ml of water added dropwise with stirring. Cooling with an ice bath produced a large quantity of solid which was collected by filtration and dried under vacuum. The solid was dissolved in 40 ml of acetonitrile, 3 ml of water added, and the mixture warmed to dissolve some precipitated material. Cooling to room tem-

perature produced yellow crystals. An elemental analysis indicated that the crystal chosen for study was not representative of the bulk of the crystalline solid. The crystal consists of discrete molecules of Th(NO₃)₂(BMPP)₂(OPPh₃)₂ which gives a calculated analysis (for C₇₀H₅₆N₆O₁₂P₂Th) of C 57.30, H 3.85, N 5.73, P 4.22%; the values found for the bulk sample were: C 62.38, 62.47; H 4.52, 4.45; N 6.91, 7.01; P 2.74, 2.77% (Galbraith Laboratories, Inc.).

A parallelepiped of approximate dimensions 0.3 × 0.2 × 0.2 mm was used for the diffraction study. Enraf-Nonius CAD-4 diffractometer; graphite monochromator; lattice parameters from 25 reflections (10 ≤ θ ≤ 16°). An absorption correction was made by measuring the intensity of a low-angle reflection as a function of ψ (mapped to φ in the actual correction), normalizing to the ψ = 0 value and superimposing a spherical correction, assuming a radius which is the average of the three most prominent directions of crystal development to (*r* = 0.2 mm) transmission = 0.58–0.41. Variable speed θ–2θ scans [to σ(*I*)/*I* = 0.02 or 90 s], 2θ_{max} = 45°, *h* = 0 to 12, *k* = 0 to 25, *l* = 0 to 26, 4528 total reflections, 2744 for which *I* ≥ 2σ(*I*), *R*_{int} = 1.5% (9056 reflections), two standard reflections, no systematic variation during data collection. The structure was solved using standard Patterson and difference Fourier methods and a full-matrix least-squares refinement. Calculations were carried out on a Cray1 computer using the *Los Alamos Crystal Structure System*, developed primarily by A. C. Larson; anisotropic temperature factors for atoms heavier than H and a secondary-extinction factor (not significantly > 0) (Zachariasen, 1967; Larson, 1967). Least squares† minimized Σ*w*(Δ*F*)², *w* = [σ_{*c*}²(*F*) + 0.03*F*²]⁻¹, σ_{*c*}²(*F*) based on counting statistics, *R*(*F*) = 5.8%, *wR* = 8.8%, *S* = 3.8, (Δ/σ)_{max} = 1 × 10⁻². Final Δ*F* Fourier synthesis 1.9 > ρ >

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53042 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional coordinates and equivalent isotropic thermal parameters

$$B_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Th(1)	0.12904 (7)	0.00000	0.25000	3.1
N(1)	-0.0164 (19)	-0.0624 (8)	0.1687 (10)	6.9
O(3)	-0.0484 (12)	-0.0515 (7)	0.2159 (7)	6.4
C(1)	0.1766 (16)	-0.1456 (8)	0.2599 (8)	4.1
C(3)	0.3237 (20)	-0.2234 (9)	0.2573 (12)	8.1
C(5)	0.3203 (30)	-0.2862 (11)	0.1740 (14)	9.7
C(7)	0.1769 (23)	-0.2091 (10)	0.1836 (11)	7.3
C(9)	0.0706 (19)	-0.2063 (10)	0.3286 (8)	5.5
N(2)	-0.0050 (18)	-0.1935 (7)	0.3641 (8)	7.0
C(11)	-0.1041 (18)	-0.1078 (11)	0.3996 (9)	6.5
C(13)	-0.2795 (23)	-0.1160 (17)	0.4553 (10)	10.4
C(15)	-0.1667 (24)	-0.0282 (12)	0.4527 (11)	8.1
C(17)	0.0411 (15)	-0.1106 (8)	0.3276 (7)	3.2
O(6)	0.2890 (10)	0.0083 (5)	0.1930 (5)	3.9
C(18)	0.4324 (17)	-0.0362 (8)	0.1164 (8)	3.9
C(20)	0.4222 (24)	-0.1377 (10)	0.1006 (10)	6.7
C(22)	0.5488 (19)	-0.0749 (9)	0.0459 (10)	6.4
C(24)	0.3465 (16)	0.0779 (9)	0.1122 (8)	3.7
C(26)	0.1985 (21)	0.1137 (11)	0.0494 (10)	6.9
C(28)	0.3740 (25)	0.1719 (9)	0.0727 (10)	7.7
C(30)	0.5102 (16)	0.0479 (8)	0.1920 (8)	3.8
C(32)	0.7177 (19)	0.0568 (10)	0.2082 (9)	5.6
C(34)	0.5795 (18)	0.1097 (8)	0.2623 (9)	5.6
O(1)	0.0861 (12)	-0.0484 (6)	0.1560 (6)	5.7
O(2)	-0.0807 (8)	-0.0879 (8)	0.1346 (8)	10.4
O(4)	0.1950 (10)	-0.0976 (5)	0.2422 (6)	4.1
C(2)	0.2264 (18)	-0.1954 (8)	0.2315 (9)	5.1
C(4)	0.3669 (25)	-0.2701 (13)	0.2227 (15)	10.5
C(6)	0.2183 (32)	-0.2536 (12)	0.1491 (13)	11.2
C(8)	0.1047 (17)	-0.1545 (8)	0.3046 (8)	4.5
C(10)	0.1075 (22)	-0.2665 (9)	0.3234 (9)	7.2
N(3)	-0.0262 (14)	-0.1345 (6)	0.3628 (6)	4.5
C(12)	-0.2036 (23)	-0.1424 (11)	0.4209 (11)	8.7
C(14)	-0.2562 (28)	-0.0590 (15)	0.4727 (13)	10.2
C(16)	-0.0884 (19)	-0.0508 (9)	0.4166 (9)	6.1
O(5)	0.0411 (12)	-0.0586 (5)	0.3181 (5)	3.9
P(1)	0.38808 (44)	0.02309 (21)	0.15659 (21)	3.6
C(19)	0.3880 (20)	-0.0889 (10)	0.1287 (8)	5.4
C(21)	0.5092 (21)	-0.1287 (10)	0.0605 (10)	6.4
C(23)	0.5079 (18)	-0.0275 (9)	0.0751 (8)	4.9
C(25)	0.2441 (19)	0.0709 (10)	0.0852 (10)	6.5
C(27)	0.2660 (26)	0.1637 (13)	0.0470 (9)	8.7
C(29)	0.4114 (21)	0.1252 (10)	0.1056 (10)	5.7
C(31)	0.6235 (18)	0.0325 (9)	0.1803 (8)	4.9
C(33)	0.6933 (17)	0.0939 (8)	0.2481 (12)	5.3
C(35)	0.4858 (17)	0.0860 (8)	0.2326 (8)	4.4

-1.0 e \AA^{-3} , not in chemically interpretable positions. Neutral atom scattering factors, f' and f'' from Cromer & Waber (1974) and Cromer (1974). The atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1. Relevant bond distances and angles are given in Table 2 and the numbering of the atoms is shown in Fig. 1.

Discussion. The crystal contains discrete molecules of $\text{Th}(\text{NO}_3)_2(\text{BMPP})_2(\text{OPPh}_3)_2$ with the thorium ion bound to ten O atoms of two bidentate nitrate anions, two bidentate BMPP anions, and two triphenylphosphine oxide molecules. The view shown in Fig. 1 is displaced about 15° from the twofold axis. If the nitrate anion is considered to occupy a single coordination site, the inner coordination sphere geometry can be described as distorted trigonal dodecahedral with BMPP O atoms, O(4) and O(5), representing the *A* sites, and the phosphoryl O(6) atom and the midpoint of the nitrate O(1')—O(3') vector representing the *B* sites of the interpenetrating trapezoids.

Table 2. Selected bond distances (\AA) and angles ($^\circ$)

Th—O(1)	2.68 (2)	C(8)—C(17)	1.40 (3)
Th—O(3)	2.55 (1)	C(9)—C(10)	1.50 (3)
Th—O(4)	2.45 (1)	C(9)—N(2)	1.29 (3)
Th—O(5)	2.44 (1)	N(1)—N(3)	1.42 (2)
Th—O(6)	2.36 (1)	N(3)—C(11)	1.44 (3)
O(1)—N(1)	1.28 (2)	N(3)—C(17)	1.31 (2)
O(2)—N(1)	1.20 (2)	O(5)—C(17)	1.26 (2)
O(3)—N(1)	1.27 (2)	O(6)—C(1)	1.52 (1)
O(4)—C(1)	1.24 (2)	P(1)—C(18)	1.81 (2)
C(1)—C(2)	1.50 (3)	P(1)—C(24)	1.78 (2)
C(1)—C(8)	1.42 (3)	P(1)—C(30)	1.78 (2)
C(8)—C(9)	1.43 (3)		

Inner coordination sphere		Ligand angles	
O(1)—Th—O(1')	158.6 (6)	O(1)—N(1)—O(2)	120 (2)
O(1)—Th—O(3)	49.1 (5)	O(2)—N(1)—O(3)	117 (2)
O(1)—Th—O(3')	110.7 (4)	O(2)—N(1)—O(3)	123 (2)
O(1)—Th—O(4)	65.3 (4)	O(4)—C(1)—C(2)	119 (2)
O(1)—Th—O(4')	122.3 (5)	O(4)—C(1)—C(8)	121 (2)
O(1)—Th—O(5)	107.6 (5)	C(2)—C(1)—C(8)	119 (2)
O(1)—Th—O(5')	62.7 (4)	C(1)—C(8)—C(9)	129 (2)
O(1)—Th—O(6)	130.6 (4)	C(1)—C(8)—C(17)	122 (2)
O(1)—Th—O(6')	69.1 (4)	C(9)—C(8)—C(17)	109 (2)
O(3)—Th—O(3')	71.9 (4)	C(8)—C(9)—C(10)	135 (2)
O(3)—Th—O(4)	0.752 (7)	C(8)—C(9)—N(2)	106 (2)
O(3)—Th—O(4')	137.3 (5)	C(10)—C(9)—N(2)	119 (2)
O(3)—Th—O(5)	68.0 (5)	C(9)—N(2)—N(3)	109 (2)
O(3)—Th—O(5')	72.3 (5)	N(2)—N(3)—C(11)	122 (2)
O(3)—Th—O(6)	143.5 (5)	N(2)—N(3)—C(17)	110 (2)
O(3)—Th—O(6')	188.2 (5)	C(11)—N(3)—C(17)	128 (2)
O(4)—Th—O(4')	143.5 (5)	O(5)—C(17)—N(3)	124 (2)
O(4)—Th—O(5)	69.4 (4)	O(5)—C(17)—C(8)	131 (2)
O(4)—Th—O(5')	127.9 (4)	C(8)—C(17)—N(3)	106 (2)
O(4)—Th—O(6)	73.9 (4)	O(6)—P(1)—C(18)	112 (1)
O(4)—Th—O(6')	77.5 (4)	O(6)—P(1)—C(24)	110 (1)
O(5)—Th—O(5')	130.4 (6)	O(6)—P(1)—C(30)	112 (1)
O(5)—Th—O(6)	81.5 (4)	C(18)—P(1)—C(24)	107 (1)
O(5)—Th—O(6')	144.0 (4)	C(18)—P(1)—C(30)	108 (1)
O(6)—Th—O(6')	76.0 (3)	C(24)—P(1)—C(30)	107 (1)
Th—O(1)—N(1)	93 (1)		
Th—O(3)—N(1)	100 (1)		
Th—O(4)—C(1)	142 (1)		
Th—O(5)—C(17)	134 (1)		
Th—O(6)—P(1)	171 (1)		

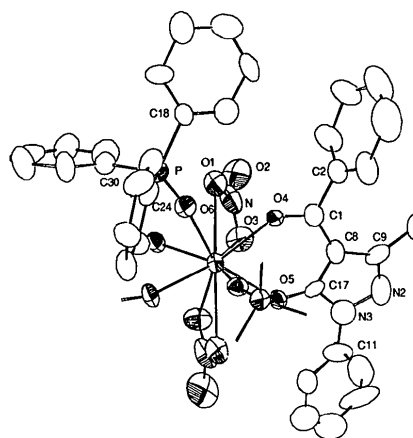


Fig. 1. ORTEP projection displaced about 15° from the crystallographic twofold axis. The phenyl rings of one phosphine oxide group and the C and N atoms of one BMPP ligand have been omitted for clarity.

The Th—O distances of the BMPP anions [Th—O(4) 2.45 (1), Th—O(5) 2.44 (1) \AA] are equal, within experimental error, in contrast to the analogous U—O and Eu—O distances in $\text{UO}_2(\text{BMPP})_2(\text{dimethyl sulfoxide})$ and $\text{Eu}(\text{BMPP})_3$.

(triisobutylphosphate)₂ which consistently show longer M—O distances with the acyl O atom, with average differences of 0.04 (1) and 0.13 (4) Å, respectively (Ryan & Jarvinen, 1987; Karaseva, Karasev, Udovenko & Sigula, 1983). The Th atom is 0.12 Å above the O—C—C—O plane of the BMPP anion, corresponding to a dihedral angle about the O(4)—O(5) vector of 3°. The largest deviations from the O—C—C—O plane are C(1) 0.027 and C(8) -0.028 Å. The acyl group is bent slightly (7°) out of the plane of the pyrazolone ring. The dihedral angle between the two O—C—C—O planes is 98.8°.

The Th atom is 0.11 Å out of the plane of the nitrate ligand. The Th—O distances of the nitrate anions [Th—O(1) 2.55 (1), Th—O(3) 2.68 (1) Å] are similar to the Th—O distances reported for a variety of thorium complexes containing nitrate ligands reviewed by Casellato, Vigato & Vidali (1981).

The Th—O distance of the phosphoryl O atom [Th—O(6) 2.36 Å] is significantly shorter than the Th—O distances of either anionic ligand. The Th—O(6) distance can be compared with those observed in Th(TTA)₄(TOPO) (2.30 Å; Leipoldt, Wessels & Bok, 1975), [Th(NO₃)₃{OP(NMe₂)₃]₄]₂[Th(NO₃)₆] (average value 2.34 Å; English, du Preez, Nassimbeni & van Vuuren, 1979), [Th(NO₃)₅(OPMe₃)₂][PPh₄] and [Th(NO₃)₃(OPMe₃)₄]₂[Th(NO₃)₆] (average values 2.34 and 2.38 Å, respectively; Alcock, Esperas, Bagnall & Hsian-Yun, 1978) [TTA = 1,1,1-trifluoro-3-(2-thenoyl)acetate, TOPO = tri-*n*-octylphosphine oxide]. The average Th-to-phosphoryl O distances in these structures are also substantially shorter than the Th—O distances of the

anionic ligands, a reflection of the strong Lewis basicity of the phosphoryl donors.

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Bis[diethyl(glycylhistidinato)tin]–Methanol (1/1)

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Abstract. C₂₅H₄₄N₈O₇Sn₂, *M_r* = 806.05, monoclinic, *P*2₁, *a* = 8.711 (4), *b* = 13.009 (5), *c* = 15.020 (6) Å, β = 102.91 (3)°, *V* = 1659 (1) Å³, *Z* = 2, *D_x* = 1.61 Mg m⁻³, *F*(000) = 812, λ(Mo *K*α) = 0.71073 Å, μ = 0.82 mm⁻¹, *T* = 291 (1) K. Final *R* = 0.035 for 5441 unique observed reflexions [*F* ≥ 3.0σ(*F*)]. The title compound contains two different Et₂SnGlyHis molecules and one MeOH molecule in the asymmetric unit. In one Et₂SnGlyHis molecule the polyhedron around the Sn atom is a distorted trigonal bipyramid with two αC(Et) atoms and N_{peptide} in

the equatorial plane and N_{amino} and O_{carboxylate} in the apical positions. In the other molecule the Sn atom attains hexacoordination with N_{amino}, O_{carboxylate} and the two αC(Et) atoms in the equatorial plane, and N_{peptide} and N_{imide} in the apical positions. The two molecules are linked by a hydrogen bond between the amino group of the pentacoordinated unit and O(=C)_{carboxylate} of the hexacoordinated unit.

Introduction. A series of diorganotin derivatives of dipeptides have been found to exhibit anti-leukaemic