

ring distances, and central-ring angles at carbon of 113–119°. The structural parameters of the present tin compound are similar to those of the equatorial isomers. Because of the poor overlap between the diffuse orbitals of Sn, As, or Sb and the compact  $\pi$  system of a phenylene group, the role of the lone-pair electrons of the heteroatoms is not likely to be the dominant factor in these structural differences. A more important factor may be the cross-ring interaction between heteroatoms. In the present tin structure the Sn...S distance is 3.35 Å, which is 0.65 Å shorter than the van der Waals separation. The equatorial heterocyclics with small dihedral angles also have short cross-ring distances: 0.73 Å shorter than van der Waals for the Sb...S distance in C<sub>12</sub>H<sub>8</sub>SSbCl, and 0.90 Å shorter for equatorial C<sub>12</sub>H<sub>8</sub>(AsMe)<sub>2</sub>. Axial C<sub>12</sub>H<sub>8</sub>SAsCl, in contrast, has an As...S distance that is only 0.32 Å shorter than the van der Waals radii and it has a flattened structure with a dihedral angle of 152°. These cross-ring interactions may, of course, be either the cause or the result of the molecular folding.

One minor structural feature of interest involves the displacement of the heteroatoms from the planes of the phenylene groups (Table 3). Heterocyclic molecules of template (II) have invariably been found to have the heteroatoms displaced (0.03–0.10 Å) from the planes of the phenylene groups, so that the heteroatoms are on the outside of the fold of the molecule. The tin compound presents an exception to this generalization: while the S atom is displaced in the normal way, the Sn atom is displaced (0.05 and 0.09 Å) from the two phenylene planes on the inside of the fold angle.

Table 3. Deviations (Å) from least-squares planes and dihedral angles (°) between planes

	Plane 1	Plane 2		Plane 3	Plane 4
Sn	-0.0001 (2)	0.0904 (2)*	Sn	-0.0002 (3)	0.0503 (3)*
S	0.006 (2)	-0.052 (2)*	S	0.014 (2)	-0.182 (2)*
C(1)	0.048 (5)	-0.009 (5)	C(7)	0.031 (5)	-0.012 (5)
C(2)	-0.024 (6)	0.005 (6)	C(8)	-0.081 (5)	0.005 (5)
C(3)	-0.062 (6)	0.006 (6)	C(9)	-0.110 (6)	0.008 (6)
C(4)	-0.018 (7)	-0.018 (7)	C(10)	-0.018 (7)	-0.015 (7)
C(5)	0.011 (7)	0.009 (7)	C(11)	0.061 (6)	-0.002 (6)
C(6)	0.049 (7)	0.007 (7)	C(12)	0.071 (6)	0.016 (6)
Dihedral angles					
(1)–(3)		126.95 (8)	(2)–(4)		128.4 (2)

\* Atoms excluded from the plane calculation.

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### (*N,N*-Dimethylformamide)tetrakis(8-quinolinolato)thorium(IV), [Th(C<sub>3</sub>H<sub>7</sub>NO)(C<sub>9</sub>H<sub>6</sub>NO)<sub>4</sub>]

BY RICHARD J. BARTON, ROBERT W. DABEKA,\* HU SHENGZHI,† LYNN M. MIHICHUK, MONICA PIZZEY, BEVERLY E. ROBERTSON‡ AND WILLIAM J. WALLACE

*Faculty of Science, University of Regina, Regina, Saskatchewan, Canada S4S 0A2*

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**Abstract.**  $M_r = 881.0$ , triclinic,  $P\bar{1}$ ,  $a = 12.186$  (2),  $b = 13.765$  (2),  $c = 12.083$  (2) Å,  $\alpha = 108.92$  (2),  $\beta = 98.30$  (2),  $\gamma = 112.92$  (1)°,  $V = 1678.58$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.755$  (4),  $D_x = 1.743$  g cm<sup>-3</sup>, Mo  $K\alpha$ , graphite monochromator,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) =$

51.84 cm<sup>-1</sup>,  $T = 295$  (2) K,  $F(000) = 860$ ,  $R$  refined to 0.076 based on 6032 independent reflections. The four 8-quinolinolato ligands are bidentate, bonding to Th through O and N with an average Th–O distance of 2.341 (10) Å and Th–N distances ranging from 2.715 (10) to 2.800 (11) Å. The dimethylformamide ligand is bonded only through O with a Th–O distance of 2.48 (1) Å. The coordination polyhedron of the Th atom has been analysed in terms of the set of dihedral angles formed by the two faces meeting at each edge and has been identified as a slightly distorted tricapped trigonal prism.

\* Present address: Division of Chemistry, National Research Council of Canada, Montreal Road M-12, Ottawa, Ontario, Canada K1A 0R6.

† Visiting scholar, Department of Chemistry, University of Xiamen, People's Republic of China.

‡ Author to whom all correspondence should be addressed.

**Introduction.** Molecular structures of addition compounds of tetrakis(8-quinolinolato)thorium(IV),  $\text{Th}(\text{ox})_4$ , have been of interest because of the uncertain nature of the bonding of the fifth ligand to  $\text{Th}(\text{ox})_4$ . A crystallographic study of (dimethyl sulphoxide)tetrakis(8-quinolinolato)thorium(IV) dimethyl sulphoxide solvate [ $\text{Th}(\text{ox})_4(\text{dmsO})_2$ ] (Singer, Studd & Swallow, 1970) showed the 8-quinolinolato ligands to be bidentate, bonding to Th through N and O, and one of the dimethyl sulphoxide molecules to be bonded to Th through the O atom.

Investigation of other compounds of composition  $\text{Th}(\text{ox})_4L$ , where  $L = N,N$ -dimethylformamide,  $N,N$ -dimethylacetamide,  $N$ -methylformamide, methyl ethyl ketone, methanol, ethanol, pyridine, quinoline and 8-chloroquinoline, have indicated coordination of the fifth ligand to Th (Dabeka, 1975). The present study was undertaken to determine the coordination and stereochemistry of Th when  $L = N,N$ -dimethylformamide (dmf).

**Experimental.** Prepared from  $\text{Th}(\text{ox})_4(\text{Hox})$  where Hox is the 8-quinolinol ligand;  $\text{Th}(\text{ox})_4(\text{Hox})$  synthesized by mixing 2.5 g of thorium nitrate tetrahydrate dissolved in 425 mL of water with Hox dissolved in a mixture of 10 mL of hydrochloric acid and 15 mL of water; solution brought to a pH of 6.1 with 100 mL of 28–30% ammonia and boiled for a few minutes until the yellow colour changed to orange; precipitate filtered, washed with hot water and dried, first over phosphoric anhydride at room temperature and then *in vacuo*, forming a yellow powder; yellow  $\text{Th}(\text{ox})_4(\text{Hox})$  dissolved in warm  $N,N$ -dimethylformamide, the resulting solution quickly filtered; yellow precipitate formed, washed with dmf and benzene;  $\text{Th}(\text{ox})_4$  dmf recrystallized by dissolving a small portion (~10 mg) of the yellow powder in a minimum amount of dmf (~10 mL); hexane (~2 mL) added and solution stored at room temperature for 6 weeks, when small plates appeared; density measured by flotation using dimethylformamide and hexane. Crystal dimensions,  $0.10 \times 0.03 \times 0.20$  mm; diffractometer, modified automated Picker FACS-I; cell parameters from fit to 95 reflections with  $2\theta$  between 4 and  $43^\circ$ ; radiation,  $\text{Mo } K\alpha$ ; three standard reflections measured after every 47 reflections, average intensity decrease over data collection, 2%;  $\theta$ - $2\theta$  scan mode;  $0^\circ < 2\theta \leq 60^\circ$ ; 9634 independent reflections measured, 6032 with  $F_o > 2\sigma(F_o)$  used in refinement; maximum  $h,k,l$  are 18, 20 and 17; no systematic absences; standard data reduction; approximate spherical absorption correction applied; mass-absorption coefficient for Th ( $110 \text{ g}^{-1} \text{ cm}^2$ ) from Roof (1959); atomic scattering factors from Cromer & Mann (1968); anomalous-scattering corrections from *International Tables for X-ray Crystallography* (1968) applied to Th;  $\sigma(F_o)$  based on counting statistics of individual reflection plus factor associated with excess scatter in standard reflections; solved by

Patterson and heavy-atom methods; refined by blocked full-matrix least squares using the XRAY system (Stewart, 1976); non-hydrogen atoms refined anisotropically, H atoms isotropically; largest residual electron density not in the vicinity of the Th atom  $1.6 \text{ e } \text{Å}^{-3}$  at  $x = \frac{1}{8}$ ,  $y = \frac{1}{2}$ ,  $z = \frac{1}{4}$ , partial O atom placed at coordinates refined to zero occupancy, assumed spurious; maximum least-squares shift/error, 0.34, average 0.02;  $wR = 0.063$ ,  $w = 1/\sigma^2(F_o)$ ,  $S = 1.65$ ; quantity minimized,  $\sum w(|F_o| - |F_c|)^2$ .

**Discussion.** Fractional atomic coordinates and thermal parameters are given in Table 1 and bond lengths and bond angles are given in Table 2. The atom-labelling sequence of the 8-quinolinolato ligands ( $n = 2, 3, 4, 5$ ) is given in Fig. 1(a) and the atom-labelling sequence of the  $N,N$ -dimethylformamide ligand is given in Fig. 1(b). Fig. 2 illustrates a stereoview of the molecule.\*

The 8-quinolinolato ligands are bonded to the  $\text{Th}^{4+}$  ion through their O and N atoms. The  $N,N$ -dimethylformamide ligand is bonded to Th through its O atom to give the  $\text{Th}^{4+}$  ion a coordination number of nine. The average Th—O distance for the 8-quinolinolato ligands of 2.341 Å is similar to the value of 2.32 Å found by Singer, Studd & Swallow (1970) in  $\text{Th}(\text{ox})_4(\text{dmsO})_2$ . The average Th—N distance is 2.754 Å in comparison with the value of 2.66 Å in  $\text{Th}(\text{ox})_4(\text{dmsO})_2$ . The significant difference in Th—N bond length and the large r.m.s. deviation within the four Th—N bond lengths observed here (0.033 Å) results from the relative weakness of the Th—N bonds and the fact that they are easily varied to accommodate the stereochemistry of the ligands.

The structure of  $\text{Th}(\text{ox})_4(\text{dmf})$  may also be compared with that of tetrakis(tropolonato)( $N,N$ -dimethylformamide)thorium(IV) [ $\text{Tht}_4(\text{dmf})$ , Day & Hoard, 1970]. The Th—O bond length to the dmf ligand is 2.48 (1) Å in  $\text{Th}(\text{ox})_4(\text{dmf})$  and 2.519 (6) Å in  $\text{Tht}_4(\text{dmf})$ . The Th—O bond lengths to the tropolonato O atom average to 2.45 Å in the latter compound. The shorter Th—O distances for the 8-quinolinolato ligands result from the presence of a greater charge on the O atoms in the 8-quinolinolato ligands than on either of the two equivalent O atoms in the tropolonato ligands.

The shorter bond length to the dmf ligand observed in the present investigation suggests a greater charge on the  $\text{Th}^{4+}$  ion here. This observation is consistent with the relative nature of the delocalization in the 8-quinolinolato and tropolonato ligands as observed in these structural studies. In the latter case, the average C—C distance between the two carbonyl groups is 1.47 Å, appropriate for an  $sp^2$  hybrid single bond (Cruickshank, 1962). The other C—C distances average

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38403 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ , for H  $\times 10^3$ ) and thermal parameters ( $\times 10^3$ , for H  $\times 10^2$ )

For non-H atoms $U_{eq} = \frac{1}{3}$ trace $\bar{U}$ .			
	x	y	z
Th	3766.5 (5)	1641.4 (4)	4181.4 (4)
N,N-Dimethylformamide, ligand 1			
O(11)	5828 (8)	1838 (8)	5128 (8)
N(11)	7730 (9)	2147 (9)	4954 (9)
C(11)	6596 (12)	1466 (10)	4848 (11)
C(12)	8233 (14)	3403 (13)	5403 (15)
C(13)	8582 (15)	1684 (14)	4577 (13)
H(11)	631 (8)	50 (8)	438 (8)
H(12)	892 (14)	379 (12)	607 (12)
H(122)	853 (19)	367 (18)	482 (18)
H(123)	756 (14)	352 (12)	566 (12)
H(131)	949 (16)	238 (15)	527 (15)
H(132)	859 (11)	179 (10)	386 (11)
H(133)	839 (11)	102 (10)	456 (9)
8-Quinolinolato, ligand 2			
O(21)	3467 (7)	-233 (7)	3050 (7)
N(21)	1379 (9)	-199 (8)	3408 (8)
C(21)	367 (13)	-149 (11)	3640 (11)
C(22)	-797 (12)	-1163 (14)	3212 (13)
C(23)	-917 (13)	-2211 (12)	2520 (12)
C(24)	165 (16)	-3344 (12)	1558 (13)
C(25)	1262 (18)	-3315 (13)	1392 (14)
C(26)	2404 (14)	-2282 (12)	1873 (12)
C(27)	2436 (12)	-1237 (9)	2555 (10)
C(28)	1305 (11)	-1254 (10)	2734 (10)
C(29)	142 (12)	-2312 (11)	2246 (10)
H(21)	43 (10)	69 (9)	411 (9)
H(22)	-155 (9)	-119 (8)	338 (8)
H(23)	-173 (11)	-298 (10)	220 (10)
H(24)	-73 (10)	-403 (9)	125 (9)
H(25)	136 (12)	-382 (11)	103 (11)
H(26)	297 (14)	-225 (13)	156 (13)
8-Quinolinolato, ligand 3			
O(31)	2346 (8)	2393 (7)	4247 (7)
N(31)	2311 (8)	1200 (8)	1975 (8)
C(31)	2301 (12)	576 (11)	868 (11)
C(32)	1632 (13)	533 (13)	-205 (11)
C(33)	1026 (12)	1184 (13)	-116 (11)
C(34)	401 (13)	2557 (13)	1239 (15)
C(35)	457 (13)	3164 (12)	2409 (15)
C(36)	1105 (13)	3141 (12)	3443 (12)
C(37)	1728 (11)	2476 (10)	3320 (11)
C(38)	1686 (11)	1849 (10)	2094 (11)
C(39)	1017 (12)	1865 (11)	1054 (11)
H(31)	245 (13)	19 (12)	89 (12)
H(32)	165 (9)	15 (8)	-106 (8)
H(33)	84 (10)	130 (9)	-76 (9)
H(34)	-3 (11)	264 (10)	65 (10)
H(35)	6 (9)	359 (8)	256 (8)
H(36)	103 (11)	352 (10)	424 (10)
8-Quinolinolato, ligand 4			
O(41)	4899 (8)	3365 (7)	3978 (7)
N(41)	5209 (9)	1622 (8)	2576 (8)
C(41)	5352 (12)	738 (10)	1874 (11)
C(42)	6251 (14)	894 (12)	1256 (12)
C(43)	7003 (12)	1954 (13)	1355 (11)
C(44)	7682 (12)	4095 (12)	2304 (12)
C(45)	7521 (13)	4945 (11)	3081 (13)
C(46)	6611 (13)	4752 (11)	3665 (13)
C(47)	5796 (11)	3642 (11)	3457 (10)
C(48)	5956 (11)	2712 (11)	2686 (10)
C(49)	6903 (12)	2936 (11)	2102 (11)
H(41)	487 (11)	5 (10)	186 (11)
H(42)	628 (7)	24 (7)	76 (7)
H(43)	743 (12)	211 (11)	99 (12)
H(44)	828 (12)	412 (11)	187 (11)
H(45)	793 (8)	562 (7)	322 (7)
H(46)	641 (9)	518 (9)	407 (9)

Table 1 (cont.)

	x	y	z	$U/U_{eq}(\text{\AA}^2)$
8-Quinolinolato, ligand 5				
O(51)	3419 (6)	1225 (6)	5863 (6)	33
N(51)	4968 (9)	3430 (8)	6464 (8)	38
C(51)	5670 (12)	4535 (11)	6744 (11)	47
C(52)	6313 (14)	5356 (11)	7966 (15)	66
C(53)	6195 (14)	5021 (12)	8880 (12)	66
C(54)	5300 (14)	3422 (13)	9566 (11)	58
C(55)	4507 (15)	2282 (13)	9225 (13)	63
C(56)	3870 (12)	1537 (11)	7984 (12)	50
C(57)	3979 (11)	1868 (10)	7030 (10)	33
C(58)	4836 (11)	3089 (11)	7396 (10)	40
C(59)	5457 (12)	3857 (11)	8650 (11)	46
H(51)	581 (12)	469 (11)	608 (11)	8 (4)
H(52)	659 (11)	600 (10)	802 (10)	7 (4)
H(53)	664 (9)	549 (8)	964 (8)	4 (3)
H(54)	580 (10)	395 (9)	1036 (9)	5 (3)
H(55)	423 (12)	205 (11)	988 (11)	9 (5)
H(56)	340 (9)	91 (8)	785 (8)	3 (3)

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

(a) N,N-Dimethylformamide, ligand 1				
Th—O(11)	2.477 (11)	C(11)—O(11)—Th	140.3 (7)	
O(11)—C(11)	1.27 (2)	O(11)—C(11)—N(11)	122.5 (12)	
C(11)—N(11)	1.29 (2)	C(11)—N(11)—C(12)	122.9 (14)	
N(11)—C(12)	1.46 (2)	C(11)—N(11)—C(13)	121.2 (12)	
N(11)—C(13)	1.47 (2)	C(12)—N(11)—C(13)	115.9 (12)	
(b) 8-Quinolinolato, ligands 2–5				
	n = 2	n = 3	n = 4	n = 5
Th—O(n1)	2.343 (9)	2.336 (11)	2.350 (9)	2.335 (9)
Th—N(n1)	2.774 (8)	2.715 (10)	2.800 (11)	2.727 (8)
N(n1)—O(n1)	2.66 (2)	2.69 (1)	2.65 (2)	2.65 (1)
N(n1)—C(n1)	1.33 (2)	1.33 (2)	1.33 (2)	1.31 (2)
C(n1)—C(n2)	1.42 (2)	1.40 (2)	1.40 (2)	1.40 (2)
C(n2)—C(n3)	1.35 (2)	1.35 (3)	1.34 (2)	1.33 (3)
C(n3)—C(n9)	1.42 (2)	1.42 (2)	1.42 (2)	1.40 (2)
C(n9)—C(n4)	1.41 (2)	1.41 (3)	1.42 (2)	1.42 (2)
C(n4)—C(n5)	1.37 (3)	1.36 (2)	1.34 (2)	1.36 (2)
C(n5)—C(n6)	1.41 (2)	1.40 (3)	1.38 (2)	1.40 (2)
C(n6)—C(n7)	1.39 (2)	1.39 (2)	1.37 (2)	1.37 (2)
C(n7)—C(n8)	1.42 (2)	1.43 (2)	1.42 (2)	1.46 (2)
C(n8)—C(n9)	1.44 (1)	1.41 (2)	1.42 (2)	1.41 (1)
C(n9)—O(n1)	1.32 (1)	1.32 (2)	1.32 (2)	1.30 (1)
C(n8)—N(n1)	1.37 (2)	1.37 (2)	1.37 (2)	1.36 (2)
N(n1)—Th—O(n1)	61.9 (3)	63.8 (3)	61.2 (3)	62.5 (3)
Th—N(n1)—C(n1)	127.1 (7)	126.7 (10)	128.4 (9)	127.9 (9)
Th—N(n1)—C(n8)	113.2 (8)	112.2 (7)	112.3 (8)	113.6 (7)
C(n1)—N(n1)—C(n8)	119.7 (9)	120.4 (12)	118.8 (12)	118.5 (9)
N(n1)—C(n1)—C(n2)	121.5 (14)	121.5 (16)	122.0 (12)	121.9 (14)
C(n1)—C(n2)—C(n3)	120.7 (15)	119.4 (13)	120.5 (15)	119.6 (13)
C(n2)—C(n3)—C(n9)	120.0 (11)	120.6 (14)	120.1 (14)	121.6 (11)
C(n5)—C(n4)—C(n9)	120.1 (12)	119.0 (17)	118.2 (14)	119.5 (11)
C(n4)—C(n5)—C(n6)	123.1 (16)	123.0 (18)	123.8 (13)	120.4 (16)
C(n5)—C(n6)—C(n7)	119.3 (17)	120.6 (13)	120.3 (14)	124.5 (13)
C(n6)—C(n7)—C(n8)	118.2 (11)	116.5 (13)	118.3 (13)	115.1 (9)
C(n6)—C(n7)—O(n1)	123.3 (14)	124.4 (12)	125.0 (13)	127.7 (10)
C(n8)—C(n7)—O(n1)	118.5 (12)	119.2 (13)	116.6 (11)	117.2 (12)
C(n7)—C(n8)—C(n9)	122.3 (12)	122.6 (14)	120.1 (12)	120.9 (13)
C(n7)—C(n8)—N(n1)	116.2 (9)	116.4 (12)	117.6 (12)	116.0 (9)
C(n3)—C(n9)—C(n4)	126.4 (12)	124.7 (15)	124.6 (14)	125.3 (10)
C(n8)—C(n9)—C(n3)	116.6 (12)	117.1 (15)	116.3 (12)	115.2 (13)
C(n8)—C(n9)—C(n4)	117.0 (14)	118.2 (13)	119.1 (14)	119.5 (11)
C(n7)—O(n1)—Th	130.1 (9)	126.1 (8)	130.6 (9)	129.7 (7)

to 1.39  $\text{\AA}$  indicating delocalization over the C<sub>7</sub> chain as opposed to over the whole ring of the tropolonato ligand. In the 8-quinolinolato ligands the absence of any unusually long bonds and the marginally longer average carbonyl bond lengths (1.32 *versus* 1.28  $\text{\AA}$  in the tropolonato ligands) suggest that the delocalization extends over the entire molecule and will therefore withdraw more negative charge from the cation.

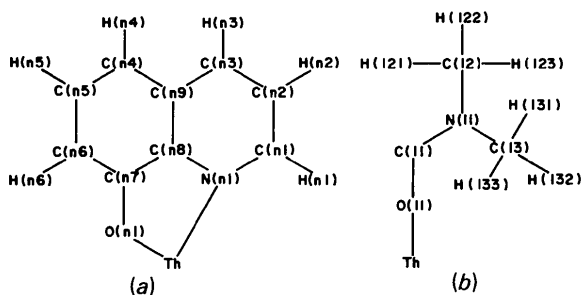


Fig. 1. Atom-labelling sequence of (a) the 8-quinolinolato ligands and (b) the *N,N*-dimethylformamide ligand.

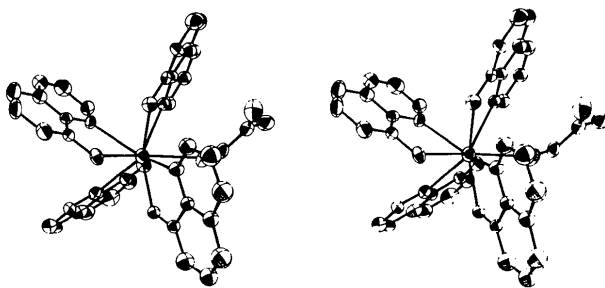


Fig. 2. Stereoview of the molecule.

It has been suggested by Porai-Koshits & Aslanov (1972) that in the case of octacoordination, a sensitive measure of polyhedral type is the set of dihedral angles formed at each edge of the polyhedron; *i.e.* the  $\delta$  parameters. The analysis has since been extended to cover a wide range of coordination numbers. We will use the nomenclature for nine-coordinate polyhedra proposed by one of our group (Robertson, 1977). The important reference polyhedra are the tricapped trigonal prism (t.t.p.) with  $D_{3h}$  ( $\bar{6}m2$ ) symmetry and the uncapped square antiprism (m.s.a.p.) with  $C_{4v}$  ( $4mm$ ) symmetry. The transition between them may be followed in terms of the  $\delta$  parameters corresponding to the three equivalent edges joining the top and bottom faces of the t.t.p. Their value in the t.t.p. is  $26.4^\circ$ . In the m.s.a.p. the  $\delta$  parameter of one of these edges goes to

zero to form the uncapped square bottom and the other two become edges of the upper capped square with  $\delta$  parameters of  $37.6^\circ$ . The three relevant edges of the polyhedron in  $\text{Th}(\text{C}_3\text{H}_7\text{NO})(\text{C}_9\text{H}_6\text{NO})_4$  have  $\delta$  parameters of  $33.2$ ,  $32.8$  and  $25.6^\circ$ . The polyhedron is clearly a t.t.p. distorted slightly towards an m.s.a.p.

The three caps of the t.t.p. are all formed by N atoms. The other N atom (from ligand 3) forms one of the end faces and thus the N—O distance (*bite* of the ligand) spans an edge of an end triangle of the t.t.p. The other three *bites* span an edge from an end to a capping atom. The unique role of ligand 3 in forming the t.t.p. is evident in Table 2. It has the largest *bite* and the shortest Th—N distance.

It would therefore appear that the capping positions (which have four neighbouring atoms in the polyhedron) are likely to be occupied by the more weakly bonding species than the end positions (which have five neighbouring atoms in the polyhedron).

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