The Structure of Tetrakis-(8-Quinolinolato)bisdimethyl sulphoxidethorium(IV)

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Summary *X*-Ray diffraction studies of $Th(C_9H_6NO)_4(Me_2SO)_2$ show that it is a nine-co-ordinate complex with a monocapped square antiprismatic structure in which one Me_2SO molecule is co-ordinated to the metal ion through its oxygen atom.

THE molecular structures of addition compounds of $Th(ox)_4$ (where ox = C_9H_6NO, the 8-quinolinolato- ligand) have attracted a certain amount of interest in the past concerning the nature of the forces binding the additional molecules to $Th(ox)_4$. Using radioactive tracer techniques and infrared spectroscopy, Corsini and Abraham[1] have shown that $Th(ox)_4$, (oxH) is nine-co-ordinate with the 8-quinolinol molecule bonded to the metal through its phenolic oxygen only. These authors also cited i.r. spectroscopic evidence to support their claim that in $Th(ox)_4$, $2Me_2SO$ the Me_2SO molecules are either held in the crystal lattice or, at best, weakly co-ordinated.

Repeated attempts to prepare suitable crystals of $Th(ox)_4$, (oxH) were unsuccessful. Recrystallisation from Me_2SO, however, produced pale yellow crystals later characterised as $Th(ox)_4,2Me_2SO$. An i.r. spectroscopic study of a sample of this material (Nujol mull) revealed a fairly strong band at $1030\ cm^{-1}$ which was assigned to $\nu(SO)$ and thought to indicate the presence of unco-ordinated Me_2SO in the crystal structure. A weaker band was found at $970\ cm^{-1}$ and from comparison with published data for $ThCl_4$, $3Me_2SO$[2] this observation is consistent with the presence of Me_2SO co-ordinated through its oxygen atom. In view of this possible ambiguity in the spectroscopic results and in order to obtain molecular parameters for $Th(ox)_4$, a full three-dimensional crystal structure analysis was done on $Th(ox)_4,2Me_2SO$. *Crystal Data*: $ThC_{40}H_{36}N_4O_6S_2$; $M = 964{\cdot}6$; pale yellow acicular crystals; monoclinic, $a = 15,917 \pm 0{\cdot}006$, $b = 15,876 \pm 0{\cdot}006$, $c = 17{\cdot}176 \pm 0{\cdot}007$ Å, $\beta = 117°54' \pm 4'$; $U = 3828{\cdot}1$ Å^3; $D_m = 1{\cdot}65 \pm 0{\cdot}01\ g\ cm^{-3}$ (flotation); $Z = 4$; $D_c = 1{\cdot}67\ g\ cm^{-3}$; $F(000) = 1896$; space group *Ia* or $12/a$; $\mu = 145{\cdot}4\ cm^{-1}$; Cu-$K_\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å); single-crystal oscillation, rotation, and Weissenberg photographs. Intensities of 2469 visually-estimated independent non-zero reflections were obtained using multiple-film equi-inclination Weissenberg photographs from levels 0—7*kl*, *hk*0—8, *h*0*l*. No corrections

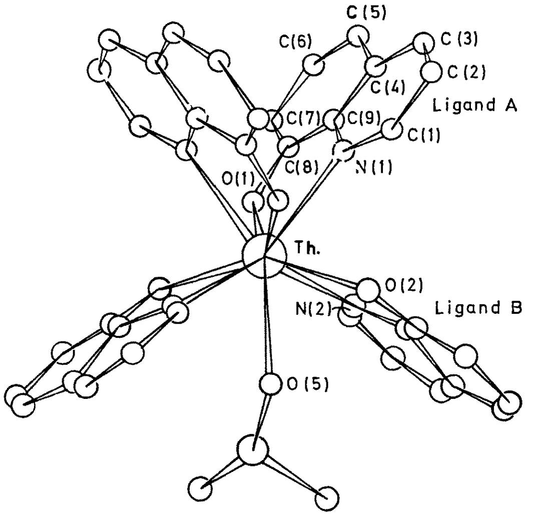

FIGURE. *The molecular structure of* Th(ox)$_4$·Me$_2$SO, *showing 2-fold symmetry of the oxine groups about the thorium atom.*

Bond lengths (Å) and bond angles (°) are given with their standard deviations in parentheses.
Thorium co-ordination.

Th–O(1)	2·32 (2)
Th–O(2)	2·32 (2)
Th–N(1)	2·62 (3)
Th–N(2)	2·70 (3)
Th–O(5)	2·47 (8)

O(1)–Th–O(2)	74·3 (0·9)
O(1)–Th–N(1)	61·9 (0·8)
O(1)–Th–N(2)	132·9 (0·7)
O(1)–Th–O(5)	112·3 (2·4)
O(2)–Th–N(1)	133·3 (0·8)
O(2)–Th–N(2)	63·0 (0·9)
O(2)–Th–O(5)	66·3 (2·2)
N(1)–Th–N(2)	143·4 (0·9)
N(1)–Th–O(5)	144·4 (3·2)
N(2)–Th–O(5)	68·4 (3·2)

Ligand distances and angles. These have been averaged between the ligands as they do not differ significantly at this stage of the refinement.

O(1)–N(1)	2·60 (3)
N(1)–C(1)	1·36 (4)
C(1)–C(2)	1·44 (7)
C(2)–C(3)	1·33 (6)
C(3)–C(4)	1·41 (6)
C(4)–C(5)	1·38 (6)
C(4)–C(9)	1·44 (5)
C(5)–C(6)	1·36 (7)
C(6)–C(7)	1·44 (7)
C(7)–C(8)	1·39 (5)
C(8)–O(1)	1·32 (5)
C(8)–C(9)	1·34 (5)

C(1)–C(2)–C(3)	118 (4)
C(8)–C(9)–C(4)	124 (3)
C(7)–C(8)–C(9)	120 (4)
C(6)–C(7)–C(8)	117 (4)
C(5)–C(6)–C(7)	122 (5)
C(4)–C(5)–C(6)	121 (5)
C(3)–C(4)–C(5)	127 (4)
C(2)–C(3)–C(4)	122 (4)
C(3)–C(4)–C(9)	116 (3)
Th–N(1)–C(1)	127 (3)
Th–N(1)–C(9)	114 (2)
C(9)–C(8)–O(1)	121 (3)
Th–O(1)–C(8)	126 (2)
C(1)–N(1)–C(9)	118 (3)
C(5)–C(4)–C(9)	115 (4)
C(7)–C(8)–O(1)	119 (3)
C(4)–C(9)–N(1)	121 (3)
C(8)–C(9)–N(1)	114 (3)
N(1)–C(1)–C(2)	123 (4)

were made for absorption or extinction. Dispersion corrections were applied to the scattering factors of thorium.[3]

The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares using a modified form of Busing, Martin, and Levy's ORFLS program.[4] Anisotropic temperature factors were used for thorium, while all other atoms were assumed to be vibrating isotropically: $R = 10{\cdot}6\%$.

The molecular structure of Th(ox)$_4$(Me$_2$SO)$_2$, together with significant bond lengths and angles, is shown in the Figure. The oxine rings are arranged in a square antiprismatic configuration about the metal ion with a two-fold axis through the thorium perpendicular to the xz plane: only one Me$_2$SO is co-ordinated. The oxine ligands are planar within experimental error with the thorium atom lying in the same plane as ligand A, but 0·61 Å above the plane of ligand B. In each case, however, the Th–N bond is longer than Th–O suggesting that co-planarity with the acceptor atom is not a rigorous criterion in assessing donor atom distances. Since Th^{IV} has been classified as a "hard acid"[5] rationalisation of the Th–N, Th–O bond lengths is essentially that given for TiCl$_2$(ox)$_2$.[6] It is certainly unlikely that any *trans*-effect is operating in Th(ox)$_4$.

Refinement of the Me$_2$SO molecules has been greatly hindered by "inverse overlap," a consequence of the centrosymmetric arrangement of Th(ox)$_4$ in the crystal structure. The overall centrosymmetry is destroyed by the Me$_2$SO molecules which would have to adopt strained planar conformations for the crystal structure to be centrosymmetric. It was thus concluded that the space group is *Ia*.

At the present stage of refinement it is not possible to calculate accurate bond lengths for either Me$_2$SO molecule. The Th–O distance for the co-ordinated Me$_2$SO stands at 2·47 ± 0·08 Å which compares favourably with solvent of crystallisation values for Th(NO$_3$)$_4$ 5H$_2$O[7] in which the bond lengths are Th–O (water) 2·438 and 2·473 Å; Th–O (nitrate) distance range between 2·528 and 2·618 Å. The orientations of the Me$_2$SO molecules are such as to suggest the possibility of hydrogen-bonding between the unco-ordinated oxygen atom and the methyl carbons of the co-ordinated molecule. Efforts are being made to overcome the problem of "inverse overlap" and full details of the analysis and refinement will be given elsewhere.

The results of this structure investigation suggest that the postulated nine-co-ordination of Th in Th(ox)$_4$,(oxH) is feasible and since the ring bite of the tropolone anion (tr$^-$) is of the same order of magnitude as that of ox$^-$ it appears likely that Th(tr)$_4$Me$_2$SO[8] is of similar structure to Th(ox)$_4$Me$_2$SO.

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