Thorium Complexes with Bidentate Ligands. Crystal Structure of Methanoltetrakis(1,2-dioxo-pyridinato)thorium(IV)

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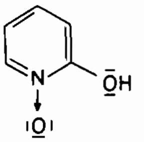
The X-ray crystal structure of the title compound has been determined from diffractometer data. The substance crystallizes in the triclinic system, space group $P\bar{1}$, *with* a = *10.13(1),* b = *13.89(1),* c = *9.47(1)* Å, α = *82.85(3),* β = *117.14(3) and* γ = *107.05(3)°;* D_c = *2.06 g* cm^{-3} *for Z = 2. The final conventional* R *was 0.052 based on the 5986 observed reflexions. Four bidentate ligands and one methanol molecule are bonded to thorium to form a distorted monocapped square antiprismatic coordination polyhedron. The Th–O bond of 2.58* Å *to the uncharged solvent molecule is significantly longer than the eight Th–O(L) bond distances (mean 2.45* Å*).*

Introduction

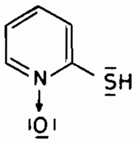
The ability of the actinide ions to coordinate pyridine N-oxide and its substituted derivatives to form stable compounds has been extensively proved [1]. Bonding of these neutral monodentate ligands is achieved through the oxygen atom and some correlations have been put forward between the basicity of the ligand and the shift of the νNO stretching band upon coordination [2].

We have extended the study to complexes of U(VI), Th(IV), and La(III) with a series of bidentate ligands: (I), (II), and (III), derived from pyridine N-oxide.

It is known that thorium, having the largest ionic radius among the actinide ions with oxidation number +4, can easily reach c.n. 8 in complexes with six-membered chelate ligands, and c.n. 9 or 10 in complexes with five-membered chelate ligands. This paper describes the preparation of Th complexes with (I), (II), (III), and the crystal structure of Th(1,2-dioxo-pyridinato)$_4$MeOH.



I



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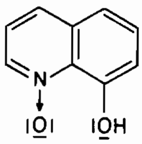

III

Experimental

Methanoltetrakis(1,2-dioxo-pyridinato)thorium(IV)

$Th(NO_3)_4 \cdot 5H_2O$ (570 mg, 1 mmol) in methanol was added to a methanolic solution of *o*-hydroxypyridine-N-oxide (444 mg, 4 mmol) and the resulting colorless solution was refluxed for two hr and reduced in volume. On adding diethylether a white product precipitated out, which, according to the elemental analysis, can be formulated as ThL_3OH. The mother liquor, on standing overnight at room temperature, deposited colorless crystals of ThL_4MeOH, suitable for the X-ray work. *Anal.* $ThL_3OH(ThC_{15}H_{13}O_7N_3)$. Calcd.: C, 31.08; H, 2.24; N, 7.25. Found: C, 31.40; H, 2.20; N, 8.34%.

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TABLE I. Atomic Parameters with Estimated Standard Deviations in Parentheses.

Atom	x	y	z	U ($\times 10^2$)
Th	0.0504(0)	0.2970(0)	0.1714(0)	*
O(1)	0.2948(9)	0.2505(6)	0.2804(10)	*
O(2)	0.0755(10)	0.1848(7)	0.0085(10)	*
O(3)	−0.0332(11)	0.1226(6)	0.2394(11)	*
O(4)	0.0577(9)	0.2693(6)	0.4348(9)	*
O(5)	−0.1444(9)	0.3060(8)	−0.0959(10)	*
O(6)	−0.2174(9)	0.2630(7)	0.1342(10)	*
O(7)	0.0087(9)	0.4579(6)	0.2164(10)	*
O(8)	0.2719(8)	0.4174(6)	0.3589(10)	*
O(9)	0.1498(10)	0.4230(7)	−0.0053(10)	*
N(1)	0.2962(12)	0.2736(8)	0.2125(13)	3.5(2)
N(2)	0.9248(13)	0.1037(8)	0.3554(13)	3.7(2)
N(3)	0.7081(11)	0.2870(7)	0.8714(12)	3.0(2)
N(4)	0.1106(11)	0.5072(7)	0.3486(12)	3.0(2)
C(1)	0.1835(12)	0.1389(8)	0.0761(12)	2.3(2)
C(2)	0.1784(15)	0.0556(10)	0.0044(15)	3.5(2)
C(3)	0.2993(17)	0.0078(11)	0.0778(18)	4.3(3)
C(4)	0.4237(17)	0.0462(11)	0.2249(18)	4.4(3)
C(5)	0.4247(16)	0.1309(11)	0.2958(17)	4.1(3)
C(6)	−0.0243(12)	0.1805(8)	0.4606(13)	2.6(2)
C(7)	0.9436(16)	0.1654(10)	0.5924(16)	4.0(3)
C(8)	0.8518(18)	0.0708(12)	0.6073(18)	4.6(3)
C(9)	0.7964(17)	−0.0063(11)	0.4968(18)	4.4(3)
C(10)	0.8301(16)	0.0108(10)	0.3677(16)	3.9(3)
C(11)	0.6738(13)	0.2655(8)	−0.0037(13)	2.7(2)
C(12)	0.5161(16)	0.2497(11)	0.9632(17)	4.0(3)
C(13)	0.4050(19)	0.2582(12)	0.8091(19)	4.9(3)
C(14)	0.4460(18)	0.2786(12)	0.6838(19)	4.8(3)
C(15)	0.6024(17)	0.2909(11)	0.7175(18)	4.3(3)
C(16)	0.2512(11)	0.4841(7)	0.4258(12)	2.1(2)
C(17)	0.3642(15)	0.5295(10)	0.5667(15)	3.4(2)
C(18)	0.3358(15)	0.6028(10)	0.6356(16)	3.6(3)
C(19)	0.1928(15)	0.6281(10)	0.5567(15)	3.6(3)
C(20)	0.0851(14)	0.5797(9)	0.4164(15)	3.2(2)
C(21)	0.3056(22)	0.4579(14)	0.0093(23)	6.3(4)

*Anisotropic thermal parameters ($\times 10^2$) in the form: $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}kla^*c^* + U_{23}klb^*c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Th	1.61(1)	2.54(2)	2.29(2)	0.59(1)	0.90(1)	−0.03(1)
O(1)	1.8(4)	3.9(5)	3.7(4)	0.8(3)	0.5(3)	−1.8(4)
O(2)	3.0(4)	4.0(5)	3.1(4)	1.8(4)	1.2(3)	−0.3(3)
O(3)	5.1(5)	2.9(4)	4.2(5)	1.3(4)	3.3(4)	0.5(4)
O(4)	2.6(4)	3.1(4)	2.9(4)	0.7(3)	1.5(3)	0.2(3)
O(5)	1.7(4)	6.0(6)	3.0(4)	0.8(4)	1.1(3)	0.7(4)
O(6)	2.5(4)	5.0(5)	2.7(4)	1.3(4)	1.3(3)	0.5(4)
O(7)	2.0(3)	2.8(4)	3.3(4)	1.0(3)	0.6(3)	−0.4(3)
O(8)	1.9(3)	3.2(4)	3.4(4)	0.8(3)	0.9(3)	−1.0(3)
O(9)	2.7(4)	4.2(5)	3.5(4)	0.7(4)	1.5(4)	1.1(4)

Atom	x	y	z
H(2)	0.0893	0.0294	−0.0995
H(3)	0.2967	−0.0521	0.0268
H(4)	0.5107	0.0141	0.2789

(continued on facing page)

TABLE I. *(continued)*

Atom	x	y	z
H(5)	0.5112	0.1594	0.4000
H(7)	1.0443	0.2048	0.5944
H(8)	0.8261	0.0583	0.6994
H(9)	0.7322	−0.0737	0.5099
H(10)	0.7868	−0.0428	0.2851
H(12)	0.5518	0.2453	1.0808
H(13)	0.2966	0.2501	0.7883
H(14)	0.3669	0.2836	0.5725
H(15)	0.6344	0.3026	0.6299
H(17)	0.4648	0.5116	0.6204
H(18)	0.4165	0.6362	0.7388
H(19)	0.1718	0.6795	0.6027
H(20)	−0.0157	0.5975	0.3603

TABLE II. Bond Distances (Å).

(a) Coordination polyhedron. E.s.d.s are 1×10^{-2} Å.

Th–O(1)	2.46	Th–O(5)	2.41
Th–O(2)	2.46	Th–O(6)	2.48
Th–O(3)	2.43	Th–O(7)	2.51
Th–O(4)	2.45	Th–O(8)	2.43
		Th–O(9)	2.58

(b) Ligands[a]. E.s.d.s are 2×10^{-2} Å or less.

O(1)–N(1)	1.32	O(3)–N(2)	1.32
O(2)–C(1)	1.30	O(4)–C(6)	1.34
C(1)–N(1)	1.30	C(6)–N(2)	1.36
O(5)–N(3)	1.35	O(7)–N(4)	1.31
O(6)–C(11)	1.27	O(8)–C(16)	1.30
C(11)–N(3)	1.35	C(16)–N(4)	1.38
		O(9)–C(21)	1.45

[a] Other distances in the rings have the usual values.

TABLE III. Bond Angles (°).

(a) Coordination. E.s.d.s are 0.3 degrees.

O(1)–Th–O(2)	62.8	O(5)–Th–O(8)	134.9
O(3)–Th–O(4)	64.1	O(6)–Th–O(8)	125.4
O(5)–Th–O(6)	63.1	O(2)–Th–O(3)	70.2
O(7)–Th–O(8)	62.9	O(2)–Th–O(5)	72.7
O(1)–Th–O(8)	65.0	O(3)–Th–O(6)	71.6
O(4)–Th–O(8)	70.0	O(1)–Th–O(3)	80.0
O(9)–Th–O(8)	76.1	O(4)–Th–O(6)	72.9
O(1)–Th–O(4)	88.1	O(2)–Th–O(9)	77.9
O(1)–Th–O(9)	87.0	O(5)–Th–O(9)	66.1
O(4)–Th–O(7)	78.6	O(1)–Th–O(7)	127.7
O(7)–Th–O(9)	77.1	O(4)–Th–O(9)	144.9
O(5)–Th–O(7)	84.8	O(3)–Th–O(5)	102.4
O(2)–Th–O(8)	122.1	O(2)–Th–O(6)	112.4
O(3)–Th–O(8)	122.6	O(6)–Th–O(7)	71.2

(b) Ligands. E.s.d.s are 1 degree or less.

Th–O(1)–N(1)	117	Th–O(3)–N(2)	118
Th–O(2)–C(1)	118	Th–O(4)–C(6)	117
O(1)–N(1)–C(1)	120	O(3)–N(2)–C(6)	117
O(2)–C(1)–N(1)	118	O(4)–C(6)–N(2)	118
Th–O(5)–N(3)	121	Th–O(7)–N(4)	116
Th–O(6)–C(11)	120	Th–O(8)–C(16)	119
O(5)–N(3)–C(11)	117	O(7)–N(4)–C(16)	117
O(6)–C(11)–N(3)	119	O(8)–C(16)–N(4)	117
Th–O(9)–C(21)	128		

Alternatively, when $Th(NO_3)_4 \cdot 5H_2O$ (570 mg, 1 mmol) in methanol was added to a methanolic solution of *o*-hydroxypyridine-N-oxide (666 mg, 6 mmol) and LiOH (144 mg, 6 mmol), a white powder precipitate of $ThL_4 \cdot 2H_2O$ was obtained.

Recrystallization of $ThL_4 \cdot 2H_2O$ from MeOH/OEt_2 gave crystals of ThL_4MeOH. $ThL_4 \cdot 2H_2O$ as well as ThL_4MeOH rapidly dissolve in dimethylsulphoxide(dmso), giving, after 2 days, crystals of $ThL_4 \cdot$ 2dmso. From IR spectra this complex can be best formulated as $[ThL_4(dmso)] \cdot$dmso. In fact a band at 1000 cm^{-1} can be ascribed to the S–O stretching frequency of a coordinated molecule, whereas a second band at 1025 cm^{-1} is probably due to the uncoordinated dmso.

Anal. $ThL_4 \cdot 2H_2O$ ($ThC_{20}H_{20}O_{10}N_4$). Calcd.: C, 33.89; H, 2.82; N, 7.90. Found: C, 33.18; H, 2.39; N, 8.37%.

Aquatetrakis(1-oxo-2-thio-pyridinato)thorium(IV)

$Th(NO_3)_4 \cdot 5H_2O$ (570 mg, 1 mmol) in methanol was added to a methanolic solution of *o*-mercaptopyridine-N-oxide (528 mg, 4 mmol) and LiOH (96

TABLE IV. Least-Squares Planes and Deviations (Å) of Individual Atoms. The Equations of the Planes are in the form AX + BY + CZ = D, where X, Y, and Z are the Fractional Coordinates of the Atoms in the Direct Cell.

Plane 1: O(1), O(4), O(7), O(9)
4.260X + 7.080Y + 3.351Z = 3.800 Å
[O(1) 0.17, O(4) −0.19, O(7) 0.20, O(9) −0.18, O(8)[a] 1.52, Th[a] −0.91]

Plane 2: O(2), O(3), O(5), O(6)
3.601X + 8.234Y + 3.327Z = 1.755 Å
[O(2) 0.07, O(3) −0.07, O(5) −0.07, O(6) 0.07, Th[a] 1.44]

Plane 3: Th, O(1), O(2), N(1), C(1)
5.015X + 7.859Y − 5.995Z = 1.648 Å
[Th −0.09, O(1) 0.12, O(2) 0.13, N(1) −0.07, C(1) −0.09]

Plane 4: Th, O(3), O(4), N(2), C(6)
1.336X + 10.695Y + 3.712Z = 3.574 Å
[Th 0.03, O(3) −1.42, O(4) 1.00, N(2) 0.09, C(6) 0.03]

Plane 5: Th, O(5), O(6), N(3), C(11)
0.208X + 13.198Y − 0.139Z = 3.759 Å
[Th 0.15, O(5) 0.26, O(6) −0.35, N(3) 0.05, C(11) −0.11]

Plane 6: Th, O(7), O(8), N(4), C(16)
−5.106X − 5.225Y + 7.853Z = −0.579 Å
[Th 0.12, O(7) −0.16, O(8) −0.17, N(4) 0.10, C(16) 0.11]

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[a] Atom non included in the plane calculation.

mg, 4 mmol). The grey precipitate obtained was stirred for 4 hr, filtered, washed with MeOH, and dried *in vacuo*. The same compound ThL$_4$H$_2$O was obtained using an excess of the ligand and of LiOH (6 mmol).

Anal. ThL$_4$·H$_2$O ($ThC_{20}H_{18}O_5S_4N_4$). Calcd.: C, 31.83; H, 2.38; N, 7.42. Found: C, 31.46; H, 2.04; N, 7.29%.

Aquatetrakis(1-oxo-8-quinolinolato)thorium(IV)

$Th(NO_3)_4 \cdot 5H_2O$ (570 mg, 1 mmol) in methanol was added to a methanolic solution of 1-oxo-8-quinolinol (444 mg, 4 mmol) and LiOH (96 mg, 4 mmol). The yellow precipitate was stirred for 4 hr, washed with MeOH, and dried *in vacuo*. The compound is insoluble in dmso and can be recovered unchanged by filtration from this solvent.

Anal. ThL$_4$·H$_2$O ($ThC_{36}H_{26}O_9N_4$). Calcd.: C, 48.53; H, 2.92; N, 6.29. Found: C, 48.79; H, 3.09; N, 6.12%.

Intensity Data

Cell parameters of [ThL$_4$MeOH] were determined by least squares from 2θ values for 25 strong reflections, measured on a four-circle diffractometer with MoKα radiation. Crystal data are: $C_{21}H_{20}O_9N_4Th$, FW = 704, $F(000)$ = 672, triclinic, space group $P\bar{1}$, with a = 10.13(1), b = 13.89(1), c = 9.47(1) Å, α = 82.85(3), β = 117.14(3), γ = 107.05(3)°, V = 1134 Å^3; D_c = 2.06 g cm^{-3} for Z = 2, and μ(MoKα) = 61.1 cm^{-1}. Integrated intensities were measured at room temperature for 6425 non-symmetry-related reflections with $\sin\theta/\lambda < 0.70$ Å^{-1} using $\theta/2\theta$ scans. Of these, 5986 had $I > 3\sigma(I)$ and were considered observed. The intensities were corrected for Lorentz and polarization and for absorption [3].

Crystal stability was monitored by periodically measuring two standard reflections; there was no evidence of crystal deterioration.

Structure Analysis

The Th position was determined by the heavy-atom method, and all other atoms from difference maps. The final R of 0.052 was obtained by full-matrix refinement with anisotropic thermal parameters for Th and O, and isotropic thermal parameters for N and C. The H atoms were introduced in calculated positions (C–H = 1.00 Å, U_{iso} = 0.06 Å^2). Scattering factors of Cromer and Mann [4] were used for non-hydrogen atoms and those of Stewart, Davidson & Simpson [5] for hydrogen. A dispersion correction of $\Delta f'$ = −7.18 and $\Delta f''$ = 8.38 was applied to Th [6]. The calculations were performed with the X-Ray system [7]. Final atomic parameters are listed in Table I. Bond lengths and angles are given in Tables II and III, and the equations of selected means planes in Table IV.

Discussion

As shown in Fig. 1 the molecular thorium complex [ThL$_4$MeOH] is a nine-coordinate chelate with eight of the coordinated oxygen atoms contributed by the four monoanionic bidentate ligands and the ninth coordinated oxygen atom contributed by the methanol. With reference to Figs. 2 and 3 the coordination polyhedron is a distorted monocapped square antiprism with O(8) as cap. The thorium atom lies only 0.91 Å below the base of the pyramidal cap, but 1.44 Å above the base of the coordination polyhedron. The mean planes for the atoms comprising the two 'square' bases are only approximately parallel, with 5.7° between their normals. The angles subtended at thorium are spread over a large set of values but the four angles subtended by the chelated ligands range from 62.8 to 64.1, averaging 63.2°; it is noteworthy that this value is very near to the mean of 62.5° of the corresponding angles subtended by the tropolonato ligands in the nine-coordinate [ThT$_4$(DMF)] [8]. The four O···O bites of the ligands range from 2.56

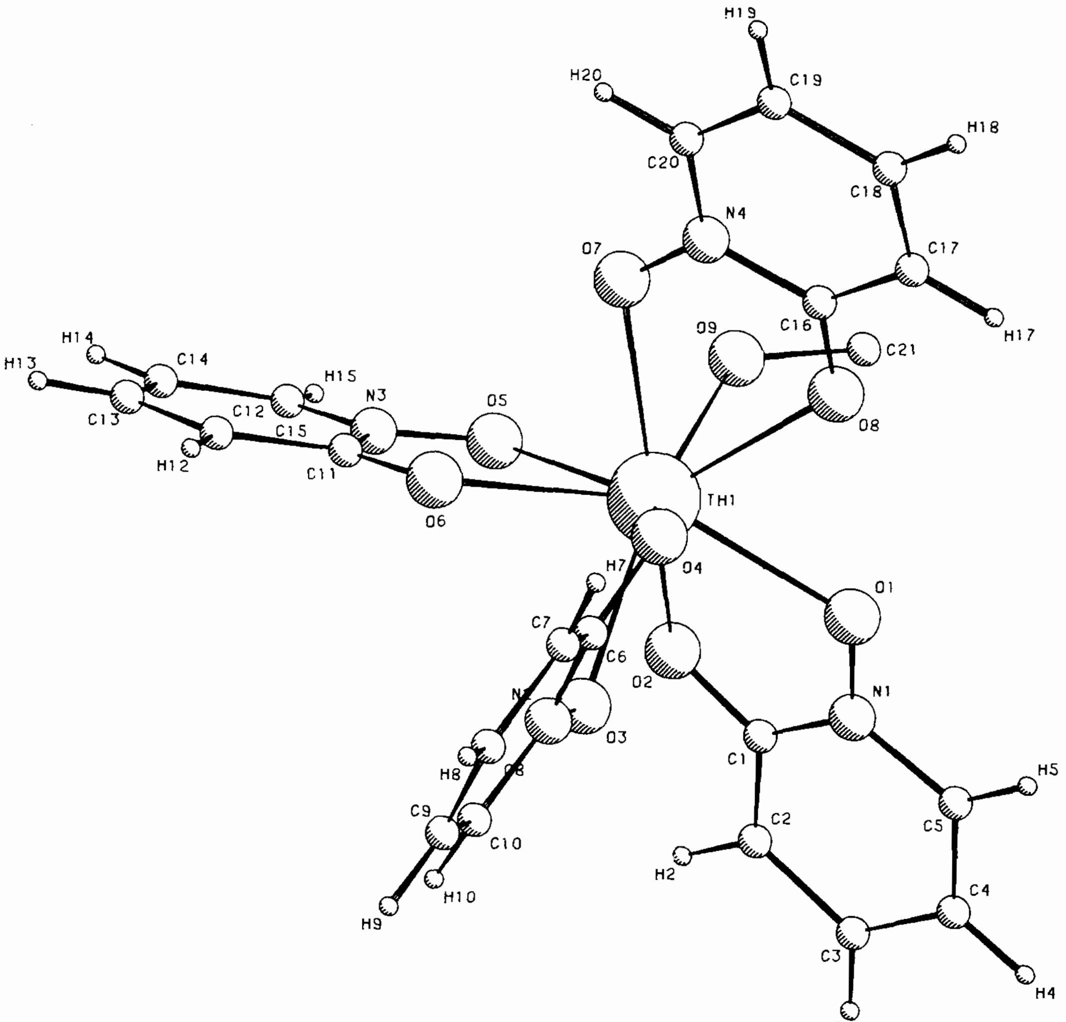

Fig. 1. The molecular structure of ThL_4MeOH.

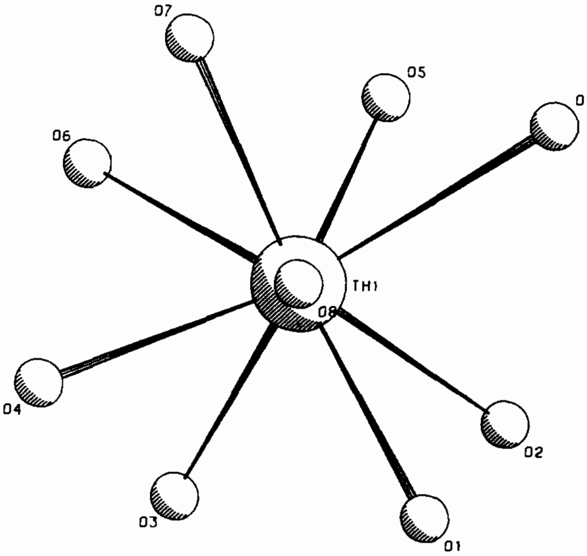

Fig. 2. The coordination polyhedron. Projection along the O(8)–Th direction.

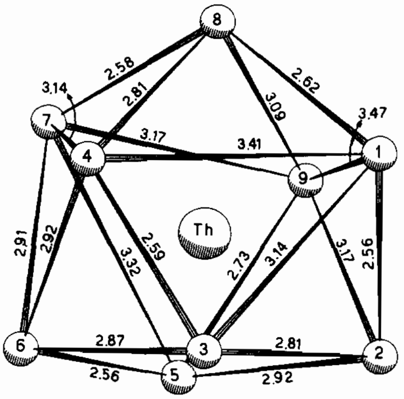

Fig. 3. The coordination polyhedron. Edge–edge distances.

to 2.59 Å. There is no indication of systematic differences between the Th–O distances relative to the same ligand and the mean of the eight Th–O(L) bond distances of 2.45 Å is the same as the mean of the Th–O(T) bond distances found in the above mentioned compound, and compares also well with the values determined in other nine-coordinated thorium complexes. The significantly longer Th–O bond of 2.58 Å to the uncharged MeOH molecule means that the solvent is weakly bonded. The N–O bond length (mean 1.32 Å) is slightly shorter than 1.35 Å found in pyridine 1-oxide [9], to which 10–20%, of double bond character was attributed [10]. This, and the mean of 1.30 Å for the C–O bond, indicate that these bonds are largely involved in the π delocalization of the negative charge that characterizes the chelating aromatic system.

Thorium compounds with (I) and (II) rapidly react with dmso to give $[ThL_4(dmso)]\cdot dmso$, while the corresponding compound with (III) is insoluble and remains unchanged. This circumstance seems to be due to the observed tendency of Th to have higher c.n. when forming complexes with five-membered chelate ligands, while it preferably forms eight-coordinate complexes with six-membered chelate ligands, as (III).

The coordination of the N–O group in all the above compounds is confirmed by the observed shift of *ca.* 45 cm^{-1} of the corresponding stretching frequency in complexes of (I) and (II), and of *ca.* 100 cm^{-1} in the complex of (III).

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