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Lanthanide and Actinide Complexes with Bidentate Ligands. Crystal Structure of Dimethylformamidetetrakis(1-oxo-2-thiopyridinato) Thorium(IV)

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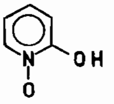
A series of uranyl(VI), thorium(IV) and lanthanum(III) complexes with bidentate chelating ligands containing oxygen and sulfur as donor atoms has been synthesized and characterized by physicochemical methods.

The crystal structure of the complex dimethylformamide-tetrakis (1-oxo-2-thiopyridinato)thorium(IV), $Th(pyOS)_4(dmf)$ has been determined from X-ray crystallography. Crystals are orthorhombic, space group $P2_12_12_1$, with $a = 10.514(6)$, $b = 11.024(7)$, $c = 24.559(10)$ Å; $D_c = 1.88$ gcm^{-1} for $Z = 4$. The final conventional R was 0.056 based on the 2354 observed reflexions. Four bidentate ligands and one dimethylformamide molecule are bonded to thorium to form a distorted monocapped square antiprismatic coordination polyhedron. The Th–S distances range from 2.94 to 2.99 Å (mean 2.97 Å). The Th–O bond distance of 2.52 Å to the uncharged solvent molecule is significantly longer than the four Th–O(pyOS) bond distances (mean 2.40 Å).

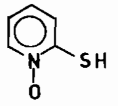
Introduction

The complexes of the actinide ions have been the subject of many structural investigations during the last years [1, 2]. These ions, owing to their large ionic radius, generally present high coordination numbers, and thorium(IV), which has the maximum ionic radius among the tetravalent actinides, can easily reach a coordination number of nine or ten with chelating ligands.

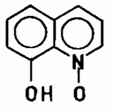
We have prepared some uranyl(VI), thorium(IV) and lanthanum(III) complexes of the type $[UO_2L_2S]\cdot xS$, $[ThL_4S]\cdot xS$ or $[ThL_4]\cdot xS$ and $[LnL_3]\cdot xS$ or $Li[LnL_4]\cdot xS$ ($x = 0$, 1), where L is the anion of the bidentate ligands:



HpyOO



HpyOS



HQuin

and S is a solvent molecule as H_2O or MeOH.

The coordinate solvent molecule in the uranyl(VI) and thorium(IV) complexes with HpyOO and HpyOS has been replaced by several more basic monodentate ligands such as Ph_3PO, dmso, dmf or dma. The present paper reports also the crystal structure of one of these complexes, $[Th(pyOS)_4dmf]$, as determined by X-ray crystallography.

Experimental

$[UO_2(pyOO)_2(H_2O)]H_2O$, $[(UO_2(pyOS)(H_2O)]\cdot H_2O$ and $[UO_2(Quin)_2(H_2O)]H_2O$ were prepared according to a literature method [3], by reaction of methanolic solutions of $UO_2(NO_3)_2\cdot 6H_2O$, the appropriate ligand, and LiOH, in a 1:1:2 molar ratio.

$[Th(pyOO)_4MeOH]$, $[Th(pyOS)_4MeOH]$ and $[Th(Quin)_4H_2O]$ were prepared, according to a literature method [4], by reaction of methanolic solution of $Th(NO_3)_4\cdot 5H_2O$, the appropriate ligand, and LiOH in a 1:4:4 molar ratio.

Preparation of Dimethylsulphoxide Bis(1-oxo-2-thiopyridinato)dioxouranium(VI)

To $UO_2(pyOS)_2\cdot 2H_2O$ (1 mmol), dissolved in MeOH, an excess of dmso was added. The solution was stirred for 3 h. An orange precipitate was obtained by addition of diethylether, washed with diethylether and dried. The precipitate was formulable as $[UO_2(pyOS)_2dmso]$. (Found: C = 20.53; H = 1.95; N = 4.02%; Calcd. for $C_{12}H_{14}O_5N_2S_3U$: C = 20.69; H = 2.01; N = 4.02%). Well-shaped crystals of $[UO_2(pyOS)_2dmso]$ were obtained from the mother liquor.

Preparation of Triphenylphosphine-oxide Bis(1-oxo-2-thiopyridinato)dioxouranium(VI)

The complex was obtained by the same procedure as was employed for $[UO_2(pyOS)_2dmso]$. (Found: C = 41.37; H = 2.90, N = 3.32%. Calcd. for $C_{28}H_{23}O_5N_2S_2PU$: C = 42.00; H = 2.87; N = 3.50%).

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Preparation of Dimethylsulphoxide Bis-(1,2-dioxopyridinato)dioxouranium(VI)

To $UO_2(pyOO)_2 \cdot 2H_2O$ (1 mmol) dissolved in MeOH an excess of dmso was added. The solution was stirred for 3 h. The orange precipitate, obtained by addition of diethylether, formulable as $[UO_2(pyOO)_2dmso]$, was washed with diethylether and dried. (Found: C = 25.86; H = 2.10; N = 5.06%. Calcd. for $C_{12}H_{14}O_7N_2SU$: C = 25.35; H = 2.46; N = 4.92%).

Preparation of Triphenylphosphine-oxide Bis-(1,2-dioxo-pyridinato)dioxouranium(VI)

The complex was obtained by the same procedure as was employed for $[UO_2(pyOO)_2dmso]$. (Found: C = 44.16; H = 2.53; N = 3.72%. Calcd. for $C_{28}H_{23}O_7N_2PU$: C = 43.75; H = 2.99; N = 3.64%).

Preparation of Bis-dimethylsulphoxide Tetrakis-(1,2-dioxo-pyridinato)thorium(IV)

$ThL_4 \cdot 2H_2O$ (or ThL_4MeOH) was dissolved in the minimum quantity of dimethylsulfoxide and stirred for two days. The white precipitate obtained by addition of diethylether was filtered, washed with diethylether and dried *in vacuo.* (Found: C = 34.17, H = 3.17, N = 6.70. Calcd. for $C_{24}H_{28}N_4O_{10}S_2Th$: C = 34.78; H = 3.38; N = 6.78%).

Preparation of Dimethylformamide Tetrakis-(1,2-dioxo-pyridinato)thorium(IV)

$ThL_4 \cdot 2H_2O$ was dissolved in dimethylformamide and stirred for 1 day. The white precipitate obtained by addition of diethylether was filtered, washed with diethylether and dried *in vacuo.* (Found: C = 36.83; H = 3.15; N = 8.93%. Calcd. for $C_{23}H_{23}N_5O_9Th$: C = 37.04; H = 3.08; N = 9.39%).

Preparation of Bis-dimethylsulphoxide Tetrakis-(1-oxo-2-thiopyridinato)thorium(IV)

$ThL_4 \cdot 2H_2O$ was dissolved in dimethylsulphoxide and stirred for two days. The white precipitate obtained by addition of diethylether was filtered, washed with diethylether and dried *in vacuo.* (Found: C = 32.56; H = 3.32; N = 6.06%. Calcd. for $C_{24}H_{28}N_4O_6S_6Th$: C = 32.28; H = 3.13; N = 6.27%).

Preparation of Dimethylformamide (1-oxo-2-thiopyridinato)thorium(IV)

$ThL_4 \cdot 2H_2O$ was dissolved in dimethylformamide and stirred for two days. The white precipitate obtained by addition of diethylether, was filtered, washed with diethylether, and dried *in vacuo.* (Found: C = 33.60; H = 2.73; N = 9.07%. Calcd. for $C_{23}H_{23}N_5O_5S_4Th$: C = 34.11; H = 2.84; N = 8.65%).

Intensity Data

Cell parameters of $[Th(pyOS)_4dmf]$ were determined by least squares from 2ϑ values for 25 strong reflexions, measured on a four-circle diffractometer with MoKα radiation. Crystal data are $C_{23}H_{22}N_5O_5S_4Th$, FW = 808, orthorhombic, $a = 10.514(6)$, $b = 11.024(7)$, $c = 24.559(10)$ Å, $V = 2846$ Å^3, $D_c = 1.88$ gcm^{-3} for $Z = 4$, F(000) = 1186; MoKα radiation, $\lambda = 0.7107$ Å; μ(MoKα) = 81.1 cm^{-1}.

The systematic extinctions h00 for h odd, 0k0 for k odd, and 00l for l odd indicated the space group $P2_12_12_1$ with the general positions x, y, z; $1/2 - x, \bar{y}, 1/2 + z$; $1/2 + x, 1/2 - y, \bar{z}$; $\bar{x}, 1/2 + y, 1/2 - z$.

Intensities were measured at room temperature for 2766 non-symmetry-related reflexions with $\sin\vartheta/\lambda < 0.70$ Å^{-1} using $\vartheta/2\vartheta$ scans. Of these, 2354 had $I > 3\sigma(I)$ and were considered observed. The intensities were corrected for Lp and for absorption [5]. Crystal stability was monitored by periodically measuring two standard reflexions; 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 0.056 was obtained by full-matrix refinement with anisotropic thermal parameters for Th, S, O, and isotropic thermal parameters for N and C. The rings H atoms were introduced in calculated positions (C–H = 1.00 Å, U iso = 0.06 Å^2). Scattering factors of Cromer & Mann [6] were used for non-hydrogen atoms and those of Stewart, Davidson & Simpson [7] for hydrogen. A dispersion correction of $\Delta f' = -7.18$ and $\Delta f'' = 8.38$ was applied to Th [8]. The calculations were performed using the X-RAY system [9]. Final atomic parameters are listed in Table I. Bond lengths and angles are given in Tables II and III, and the equations of selected mean planes in Table IV.

Results and Discussion

For the uranyl(VI) complexes prepared, a general formulation of the type $[UO_2L_2S]S$, where the coordinate solvent molecule (S) can be replaced by more basic monodentate ligands as Ph_3PO, dmso, dma or dmf, is supported by the elemental analysis as well as by the lowering of the ν(N–O) stretching frequency and by the corresponding lowering of the P–O, S–O and C–O stretching frequencies upon coordination. For these complexes a coordination number of seven, in an approximately pentagonal bipyramidal coordination geometry, can be reasonably attributed to the uranium atom, also in accordance with the structures recently determined for the complexes $[UO_2(pyOO)_2(H_2O)]H_2O$ and $[UO_2(pyOS)_2dmso]$ [3]. Thorium(IV) complexes of the type $[ThL_4S] \cdot xS$ were obtained with ligands as HpyOS and HpyOO which give rise to five-membered rings, whereas complexes of the type $[Th(Quin)_4] \cdot xS$ were obtained with the six-membered chelate ligand HQuin. The

TABLE I. Fractional Atomic Coordinates and Temperature.

Factors (Å^2 × 10^2) for [Th(pyOS)$_4$dmf]

Atom	x	y	z	U
Th	0.69233(7)	0.44592(6)	0.37655(3)	
S(1)	0.5042(6)	0.4539(6)	0.4661(2)	
S(2)	0.7226(6)	0.5416(5)	0.2635(2)	
S(3)	0.7514(6)	0.6915(5)	0.4162(3)	
S(4)	0.4914(6)	0.6226(5)	0.3502(3)	
O(1)	0.7754(13)	0.4034(15)	0.4667(6)	
O(2)	0.8066(16)	0.3160(12)	0.3169(6)	
O(3)	0.9120(13)	0.5054(12)	0.3752(7)	
O(4)	0.5092(15)	0.3709(11)	0.3293(6)	
O(5)	0.6504(16)	0.2276(12)	0.4009(6)	
N(1)	0.7079(20)	0.3566(17)	0.5084(8)	4.6(5)
N(2)	0.8722(17)	0.3450(16)	0.2702(7)	3.6(4)
N(3)	0.9799(21)	0.5926(19)	0.3998(8)	5.4(6)
N(4)	0.4382(17)	0.4294(18)	0.2934(7)	4.1(4)
N(5)	0.5438(20)	0.0494(22)	0.4130(8)	5.7(5)
C(1)	0.5822(22)	0.3724(21)	0.5146(10)	4.0(5)
C(2)	0.5270(26)	0.3207(24)	0.5598(11)	5.4(7)
C(3)	0.5954(29)	0.2533(28)	0.5973(12)	6.4(8)
C(4)	0.7243(28)	0.2348(27)	0.5876(12)	6.5(8)
C(5)	0.7842(26)	0.2860(23)	0.5434(10)	5.3(7)
C(6)	0.8404(20)	0.4458(23)	0.2408(9)	4.2(5)
C(7)	0.9065(22)	0.4648(22)	0.1930(9)	4.4(6)
C(8)	1.0006(28)	0.3822(26)	0.1767(11)	6.0(7)
C(9)	1.0295(25)	0.2845(24)	0.2060(10)	4.8(6)
C(10)	0.9640(24)	0.2643(23)	0.2547(10)	4.8(6)
C(11)	0.9114(22)	0.6832(21)	0.4252(9)	4.0(5)
C(12)	0.9821(3)	0.7751(27)	0.4539(12)	5.8(8)
C(13)	1.1157(29)	0.7611(28)	0.4541(12)	6.4(8)
C(14)	1.1836(37)	0.6745(30)	0.4220(13)	8.2(9)
C(15)	1.1077(23)	0.5875(21)	0.3980(10)	4.3(6)
C(16)	0.4164(22)	0.5557(24)	0.2989(9)	4.5(5)
C(17)	0.3344(28)	0.6077(26)	0.2587(12)	6.4(8)
C(18)	0.2884(26)	0.5432(26)	0.2163(10)	5.8(7)
C(19)	0.3180(30)	0.4144(24)	0.2116(11)	6.0(7)
C(20)	0.3890(24)	0.3619(23)	0.2509(10)	4.9(6)
C(21)	0.5630(24)	0.1504(23)	0.3862(10)	5.3(6)
C(22)	0.6189(34)	0.0212(34)	0.4623(15)	9.0(10)
C(23)	0.4432(31)	−0.0352(31)	0.3937(12)	8.1(10)

Anisotropic thermal parameters (Å^2 × 10^2).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Th	3.84(3)	2.30(3)	3.92(4)	−0.10(4)	0.31(4)	−0.04(4)
S(1)	4.9(3)	4.3(3)	5.3(3)	0.8(3)	1.2(3)	0.6(3)
S(2)	6.3(4)	3.5(3)	5.1(3)	0.5(3)	0.2(3)	1.1(3)
S(3)	5.1(3)	3.4(3)	6.1(4)	−0.1(3)	0.8(3)	−0.7(3)
S(4)	5.6(3)	3.3(3)	6.5(4)	0.4(3)	0.0(3)	−0.4(3)
O(1)	3.1(8)	7.0(11)	5.3(10)	−1.2(7)	−0.6(7)	0.0(8)
O(2)	4.9(8)	3.5(8)	5.4(9)	1.4(9)	0.6(9)	−0.2(7)
O(3)	4.8(8)	4.7(7)	3.7(7)	−0.1(7)	−2.1(8)	0.8(8)
O(4)	5.4(9)	2.0(7)	6.2(10)	−1.1(7)	−1.3(8)	0.9(7)
O(5)	7.5(12)	2.4(7)	5.9(10)	−0.2(8)	0.0(9)	0.1(7)

coordinated solvent molecule in the first two complexes can be replaced by Ph$_3$PO, dmso, dma, dmf, as supported by the elemental analysis and by the ir spectra. It must be noted that [Th(Quin)$_4$]·xS is, for instance, insoluble in dmso and remains unchanged. This behaviour seems to be ascribed to the

TABLE II. Bond Lengths (Å) for [Th(pyOS)$_4$dmf].

Coordination			
Th–S(1)	2.96(1)	Th–O(1)	2.43(2)
Th–S(2)	2.99(1)	Th–O(2)	2.37(1)
Th–S(3)	2.94(1)	Th–O(3)	2.40(1)
Th–S(4)	2.97(1)	Th–O(4)	2.40(2)
		Th–O(5)	2.52(1)
Ligands pyOS			
S(1)–C(1)	1.70(2)	O(1)–N(1)	1.35(2)
S(2)–C(6)	1.72(2)	O(2)–N(2)	1.38(2)
S(3)–C(11)	1.70(2)	O(3)–N(3)	1.34(2)
S(4)–C(16)	1.67(2)	O(4)–N(4)	1.32(2)
dmf			
O(5)–C(21)	1.30(2)	N(5)–C(22)	1.48(4)
N(5)–C(21)	1.31(3)	N(5)–C(23)	1.49(4)

Bond lengths and angles of the rings have the usual values.

TABLE IV. Selected Mean Planes for [Th(pyOS)$_4$dmf].

X, Y and Z are the fractional coordinates of the atoms in the direct cell.

Plane 1:
O(1), O(2), O(3), O(5)
$7.82X - 6.91Y + 5.66Z = 5.84$ Å
[O(1) 0.07, O(2) 0.08, O(3) −0.07, O(5) −0.07, *Th −1.38]

Plane 2:
S(1), S(2), S(3), O(4)
$7.62X - 7.23Y + 5.11Z = 2.89$ Å
[S(1) 0.05, S(2) 0.05, S(3) −0.04, O(4) −0.06, *Th 1.08, *S(4) −1.88]

*Atoms not included in plane calculations.
Angle 1–2 = 2.4°.

TABLE III. Bond Angles (°) for [Th(pyOS)$_4$dmf].

Coordination			
S(1)–Th–O(1)	64.4(4)	O(1)–O(3)–O(2)	84.6(6)
S(2)–Th–O(2)	65.5(4)	O(1)–O(5)–O(2)	85.0(6)
S(3)–Th–O(3)	63.3(4)	O(3)–O(1)–O(5)	93.2(9)
S(4)–Th–O(4)	63.4(3)	O(3)–O(2)–O(5)	96.5(9)
O(5)–Th–O(1)	70.2(5)	S(1)–O(4)–S(2)	108.8(6)
O(5)–Th–O(2)	70.0(5)	S(1)–S(3)–S(2)	88.1(5)
O(5)–Th–O(4)	69.2(5)	O(4)–S(1)–S(3)	81.7(6)
O(5)–Th–S(1)	74.6(4)	O(4)–S(2)–S(3)	80.5(5)
S(1)–Th–S(3)	82.4(2)	O(4)–S(4)–S(2)	64.0(5)
S(1)–Th–S(4)	70.5(2)	O(4)–S(4)–S(1)	67.8(6)
S(1)–Th–O(4)	80.4(4)	S(1)–S(4)–S(3)	71.1(6)
S(2)–Th–S(3)	87.7(2)	S(2)–S(4)–S(3)	76.5(5)
S(2)–Th–S(4)	68.8(2)		
S(2)–Th–O(3)	77.8(4)		
S(2)–Th–O(4)	75.9(4)		
S(3)–Th–S(4)	66.9(2)		
S(3)–Th–O(1)	78.4(4)		
O(1)–Th–O(3)	73.7(5)		
O(2)–Th–O(3)	70.7(5)		
O(2)–Th–O(4)	84.2(5)		
pyOS			
Th–S(1)–C(1)	100(1)	S(1)–C(1)–N(1)	118(1)
Th–S(2)–C(6)	99(1)	S(2)–C(6)–N(2)	120(1)
Th–S(3)–C(11)	102(1)	S(3)–C(11)–N(3)	120(1)
Th–S(4)–C(16)	101(1)	S(4)–C(16)–N(4)	116(2)
Th–O(1)–N(1)	125(1)	O(1)–N(1)–C(1)	124(2)
Th–O(2)–N(2)	129(1)	O(2)–N(2)–C(6)	120(2)
Th–O(3)–N(3)	134(1)	O(3)–N(3)–C(11)	116(2)
Th–O(4)–N(4)	127(1)	O(4)–N(4)–C(16)	120(2)
dmf			
Th–O(5)–C(21)	133(1)	C(21)–N(5)–C(22)	120(2)
O(5)–C(21)–N(5)	122(2)	C(21)–N(5)–C(23)	119(2)
		C(22)–N(5)–C(23)	121(2)

observed tendency of thorium(IV) towards higher coordination numbers in complexes with five-membered chelate ligands, while it preferably maintains the coordination number eight, when forming complexes with ligands which give rise to six-membered rings.

On the contrary Th(pyOO)$_4$·2H$_2$O or Th(PyOO)$_4$·MeOH, as well as Th(pyOS)$_4$·H$_2$O rapidly dissolve in dmso, giving rise to complexes formulable as ThL$_4$·2dmso. These complexes can be formulated, from infrared evidence, as [ThL$_4$dmso]dmso with the central metal ion ninecoordinated: a band at about 1000 cm^{-1} was assigned to the ν(S–O) stretching frequency of the coordinated molecule, whereas a second band at about 1025 cm^{-1} can be probably ascribed to the uncoordinated dmso.

For a correct knowledge of the coordination geometry of the prepared complexes, crystals of [Th(pyOS)$_4$dmf], suitable for an X-ray structural analysis, were grown from a dimethylformamide/diethylether solution. The infrared spectrum of this complex shows the ν(C–O) stretching at 1645 cm^{-1}.

As shown in Fig. 1, [Th(pyOS)$_4$dmf] is a ninecoordinate chelate with eight donor atoms contributed by the four monoanionic bidentate ligands and the ninth by the solvent molecule.

With reference to Fig. 2: the coordination polyhedron is a distorted monocapped square antiprism with S(4) as cap. The thorium atom lies 1.38 Å above the base of the polyhedron [O(1), O(2), O(3), O(5)] and 1.08 Å below the base of the pyramidal cap [S(1), S(2), S(3), O(4)]. The mean planes for the atoms comprising the two 'square' bases are approximately parallel with 2.4° between their normals. The angles subtended at thorium are spread over a large set of values, but the four angles subtended by the chelate ligands range from 63.3° to 65.5°, averaging 64.2°. The four O···S bites of the ligands range

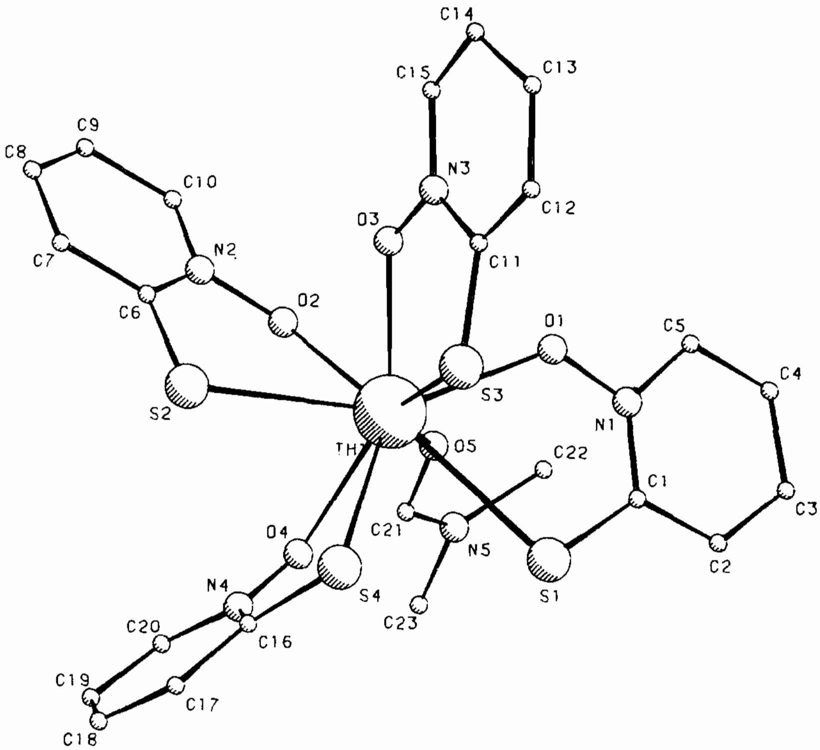

Fig. 1. The molecular structure of [Th(pyOS)$_4$dmf].

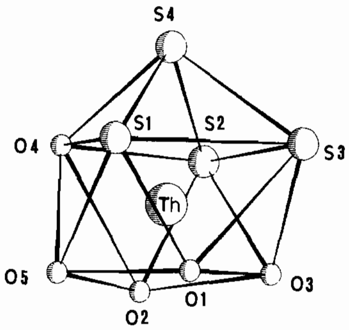

Fig. 2. The coordination polyhedron in [Th(pyOS)$_4$dmf].

from 2.84 to 2.95 Å. There are no significant differences between the Th–S distances (mean 2.97 Å) whereas the Th–O bond of 2.52 Å to the uncharged solvent molecule is significantly longer than the four Th–O(L) bond distances (mean 2.40 Å). The C–S bond (mean 1.70 Å) is double and the N–O bond length (mean 1.35 Å) is of the same order as in pyridine 1-oxide [10], to which only 10–20% of double bond character was attributed [11], showing that the negative charge of the ligand is mainly localized on the more electronegative oxygen atom. Bond distances and angles in the dmf molecule show that C(21) and N(5) are hybridized sp^2 and C(21)–O(5) and C(21)–N(5) are partial double with a statistical distribution of electron density. Apart from obvious differences in the chemical formula the structure of [Th(pyOS)$_4$dmf] strictly resembles that of [Th(pyOO)$_4$MeOH] [4]. It is noteworthy that substitution of the oxygen atom with a sulfur atom in the bidentate ligand causes a more pronounced localization of the negative charge on the strongly electronegative oxygen atom with the consequent lengthening of the N–O bond [mean 1.35 Å *vs.* 1.32 Å] and strengthening of the Th–O bond [mean 2.40 Å *vs.* 2.45 Å]. Th–O (solvent) bonds are considerably longer in both complexes. It is remarkable that the difference of *ca.* 0.5 Å between the mean value of the Th–S bonds in [Th(pyOS)$_4$dmf] and that of the Th–O(L) bonds in [Th(pyOO)$_4$MeOH] compares very well with the observed difference between the corresponding U–S and U–O bond lengths in [UO$_2$(pyOS)$_2$dmso] and [UO$_2$(pyOO)$_2$H$_2$O]·H$_2$O [3].

Most of this (~0.4 Å) must be attributed to the difference in sulfur and oxygen atom radii; the remaining 0.1 Å is probably related to the relative weakness of the metal–sulfur bond compared with the metal–oxygen bond.

The lanthanum(III) complexes are of the type LnL$_3$·xH$_2$O or Li[LnL$_4$]·xH$_2$O, and the coordination number seems most likely to be eight, even if the stoichiometry of [Ln(pyOO)$_3$H$_2$O] and [Ln(Quin)$_3$] supports coordination number seven and six respectively. In these complexes a partial oligomerization cannot be ruled out.

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