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Synthesis and characterization of new thorium and uranium phenolate complexes

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Abstract

The reaction between the chelating amino bisphenole ligand $(ONOO)H_2$ (**1**) [ONOO = $MeOCH_2CH_2N\{CH_2\text{-}(2\text{-}O\text{-}C_6H_2\text{-}Bu^t_2\text{-}3,5)\}_2$] and $(ONNO)H_2$ (**2**) [ONNO = $Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-}O\text{-}C_6H_2\text{-}Bu^t_2\text{-}3,5)\}_2$] with an excess of NaH gives the corresponding bis-sodium salts **3** and **4** quantitatively. The salts were reacted with thorium tetrachloride at room temperature to obtain the corresponding $(ONOO)ThCl_2$ (**5**) and $(ONNO)ThCl_2$ (**6**) complexes. However, $ThCl_4$ and UCl_4 react with (**3**) at higher temperatures to give the corresponding isomorphous homoleptic complexes $(ONOO)_2Th$ (**7**) and $(ONOO)_2U$ (**8**). We have also synthesized and characterized a thorium salicylaldiminato complex L_3ThCl (**11**) [L = $(C_6H_5)NCH(2\text{-}O\text{-}C_6H_2\text{-}Bu^t_2\text{-}3,5)$], in order to study the effect of the bridged ligand on the molecular structure.

Keywords: Organoactinides; Phenolate complexes; Salicylaldiminato complexes; Homoleptic complexes

1. Introduction

The substituted amino bisphenole compounds are well-known easy to modify ligands, their salts are used as dianionic precursors with early transition metals [1], late transition metals [2] and lanthanides [2]. For group 4 metals, the first generation of these ligands (ONO) (X = CH_3 in Scheme 1) mainly gave the non-reactive homoleptic complexes L_2M [3]. Two modifications were made in order to prevent the metathesis of the second ligand: (i) increasing the steric bulk of the substituents on the aryl group; (ii) attaching a donating group to the side chain terminus (X = O, N, S) to obtain the so called "second generation" ligands (ONXO); in order to induce the coordinative saturation and to avoid the activation of the second ligand. The first modification allowed the formation of $(ONO)MR_2$ complexes (M = Ti, Zr, Hf, Ta) [2,3], whereas the second modification allowed the formation of (ONXO)MR (M = Yb, Er) [2] and $(ONXO)MR_2$ (M = Ti, Zr, Hf, Ta) complexes [3–5]. Interestingly, the latter complexes were found to be highly active in various polymerization reactions [4].

The use of the salicylaldiminato ligand (**9**) also has been widely studied in the polymerization of terminal olefins [6]. It was found that the steric demand of the substituents on the phenyl groups plays a major role in the catalytic activity of these complexes; namely, the bigger the R group, the higher the activity [7].

During the last decade we have developed non-metallocene group 4 complexes and study their utilization for various catalytic processes [8,9]. In addition, we have found that metallocene complexes of the actinides are excellent catalysts for parallel demanding chemical transformations with complementary reactivities [9]. Recently, we have found that replacing the cyclopentadienyl moiety of the organoactinide metallocenes by amido groups introduced some unexpected reactivities [10,11]. Hence,

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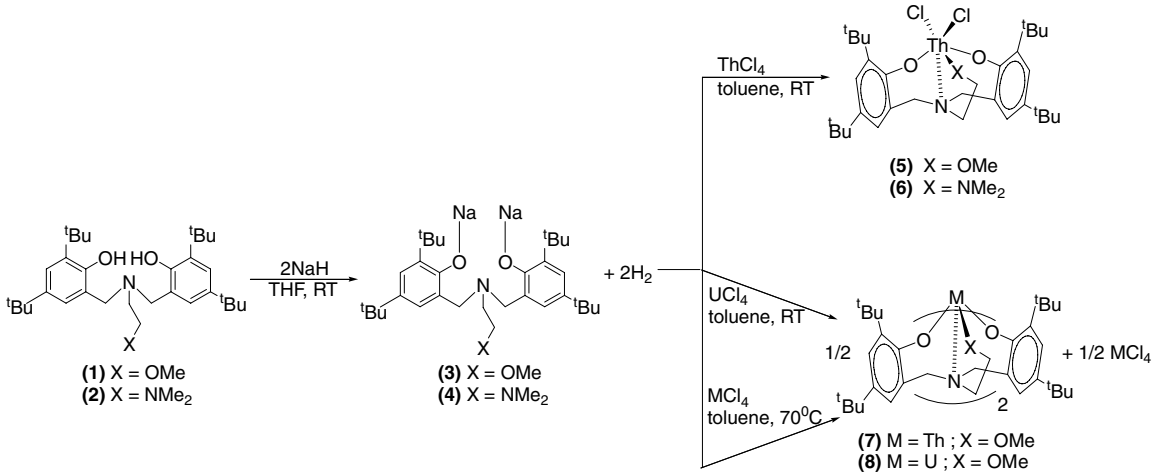


Scheme 1. Synthesis of $(ONOO)ThCl_2$, $(ONNO)ThCl_2$, $(ONOO)_2Th$ and $(ONOO)_2U$ complexes.

the introduction of new ancillary ligands in the synthesis of organoactinide complexes is expected to pioneer new catalytic processes.

Herein, we report the synthesis and structure of new actinide complexes containing the amino bisphenolate motifof the type (ONOO), and (ONNO) and the salicylaldiminato ligand.

2. Results and discussion

The sodium salt **3** [12] was prepared from **1** [3a]. The sodium salt was reacted with 1 equiv. of $ThCl_4 \cdot 3THF$ in toluene at room temperature to give complex **5** as a white solid compound (Scheme 1). The complex was isolated, recrystallized and characterized by elemental analysis and NMR spectroscopy. Our attempts to obtain suitable single crystals for X ray characterization at low temperatures with a mixture of various solvents failed due to the rapid formation of microcrystalline material. When the reaction was performed at elevated temperature (70 °C) (Scheme 1) the homoleptic complex **7** was the main product obtained as a white solid and characterized by elemental analysis, NMR and X-ray diffraction (Fig. 1). The same complex can be prepared by reacting one equivalent of the ligand salt **3** with complex **5** at 70 °C in toluene. A similar procedure was followed with UCl_4, to obtain complex **8** regardless of the ratio between the ligand and the metal. Complex **8** was isolated as a green solid and characterized by elemental analysis, NMR and X-ray diffraction (Fig. 1). The formation of complex **8** as the main product indicates that for uranium the introduction of the second ligand must be much faster than the first one. Hence, it seems plausible that the first ligand (ONOO) activates the intermediate complex $(ONOO)UCl_2$ towards complex **8**.

^{1}H NMR of complex **5** shows that the four benzylic protons split into two different sets of signals at different chemical shifts (δ 3.19 (2H) and 5.59 (2H) ppm). This NMR behavior indicates that one set of benzylic protons are interacting with the metal center more strongly, leading

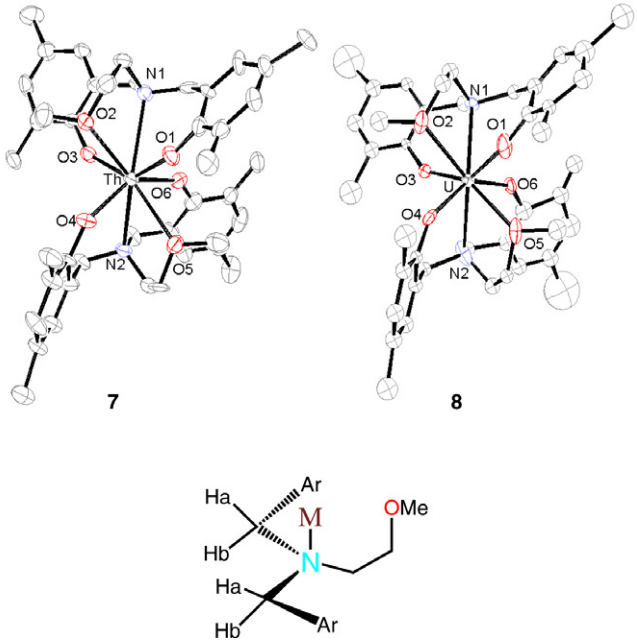


Fig. 1. ORTEP view of $(ONOO)_2Th$ (**7**) and $(ONOO)_2U$ (**8**). (Ellipsoids are presented at 50% probability.) Methyl groups of the ^{t}Bu moiety were omitted for clarity.

to a downfield shift. COSY, DEPT and HMQC spectra showed that one proton at each benzylic moiety displays agostic interaction with the metal center. This interaction leads to a stereotopic discrimination between the two protons on the same benzylic carbon. The same stereotopic feature was also observed in complex **7** having four different chemical shifts for the benzylic protons (3.22 (2H), 3.24 (2H), 5.13 (2H), 5.72 (2H) ppm).

The X-ray structures of complexes **7** and **8** corroborate our findings in solution. In both complexes the distance between the metal and the four endo protons (referred to Ha at the bottom of Fig. 1) is between 3.17 Å and 3.78 Å, whereas the distance between the metal and the exo protons (referred to Hb at the bottom of Fig. 1) is

Table 1
Selected bond lengths (Å) and angles (°) for $(ONOO)_2Th$ (**7**) and $(ONOO)_2U$ (**8**)

Complexes	7	8
M–O1	2.262(4)	2.232(11)
M–O2	2.775(7)	2.782(17)
M–O3	2.256(4)	2.202(11)
M–O4	2.233(4)	2.177(12)
M–O5	2.624(4)	2.590(14)
M–O6	2.313(4)	2.274(11)
M–N1	2.765(5)	2.707(13)
M–N2	2.725(6)	2.654(16)
O1–M–O4	102.53(18)	101.65(4)
O1–M–N1	69.86(16)	70.3(4)
O6–M–N2	71.75(17)	73.2(4)
O2–M–N1	61.17(18)	61.2(5)
N2–M–O1–O6	70.5	69.6
N2–M–O3–O4	71.4	72.1

between 3.93 Å and 4.39 Å. Suitable crystals of complexes **7** and **8** were grown from concentrated toluene solutions. Both molecular structures contain eight coordinated metal centers. The closest coordination sphere around the metals forms a tetrahedral geometry (created by the atoms O1, O3, O4, O6 in both complexes). The pendant side arm in the complexes coordinates to the thorium and uranium with bond lengths of 2.70 Å and 2.69 Å, respectively, unlike homoleptic lanthanide complexes where the side arm is not coordinated to the metal center [13]. The resemblance between the molecular structure of complexes **7** and **8** (Table 1) in the solid state indicates that the 5f electrons in complex **8** do not participate in the bonding, as expected from inner orbitals.

To understand the effect of the pendant arm donor (X) on the molecular structure, we have prepared the thorium complex of ligand **2** [5a] by reacting $ThCl_4$ with the appropriate salt **4** at room temperature. The complex $(ONNO)ThCl_2$ (**6**) was obtained and isolated as a white solid and characterized by NMR spectroscopy and elemental analysis. The high similarity between the NMR features (multiplicity and chemical shifts) of complexes **5** and **6** allows us to propose structural resemblance between these two complexes, and to conclude that the X motif do not affect much the molecular structure of the actinide complex. This result is indeed potentially important since we might expect that a metal–amine bond would be more reactive than the corresponding ether bond leaving an accessible vacant coordination site for future catalysis.

In addition, we have studied the "cooperation effect" between the two bridged phenoxy groups by synthesizing the thorium complex **11** (see Scheme 2). The complex was prepared by the reaction between one equivalent of the salicylaldiminato lithium salt [14] and $ThCl_4 \cdot 3THF$. The final complex was characterized by NMR spectroscopy and single crystal X-ray diffraction studies (Fig. 2).

Although the same metal–oxygen and metal–nitrogen interactions are present in complexes **7** and **11**, the earlier complex is eight coordinative whereas the latter is seven coordinative. The greater steric hindrance of the ligands in complex **11** impedes to introduce the fourth ligand to obtain the corresponding homoleptic complex. The single chloride atom is fixed on the Z axis with a bond length of 2.68(1) Å (compared to 2.79 Å in $[(OPhCH_2PhO)_2ThCl]^+$) [15]. The three nitrogen atoms are all located in the same plane pointing towards the chloride atom, with an average thorium–nitrogen bond length of 2.67(4) Å (compared to 2.74 Å in $(ONOO)_2Th$ and 2.68 Å in $(ONOO)_2U$). The three oxygen atoms are all located in one plane driving the *tert*-butyl groups away from the chloride atom, the average metal–oxygen bond length is 2.22(3) Å similar to 2.26 Å in $(ONOO)_2Th$ and 2.22 Å in $(ONOO)_2U$.

In conclusion, we have successfully prepared and characterized two dichloride thorium complexes (**5** and **6**) and two homoleptic thorium (**7**) and uranium (**8**) complexes.

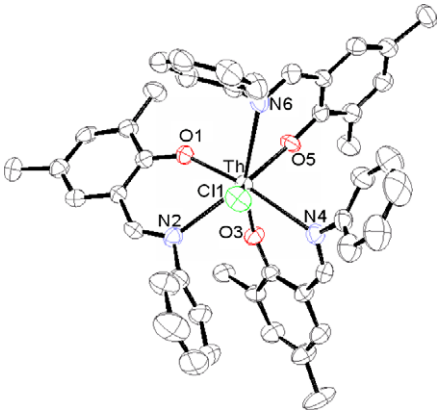
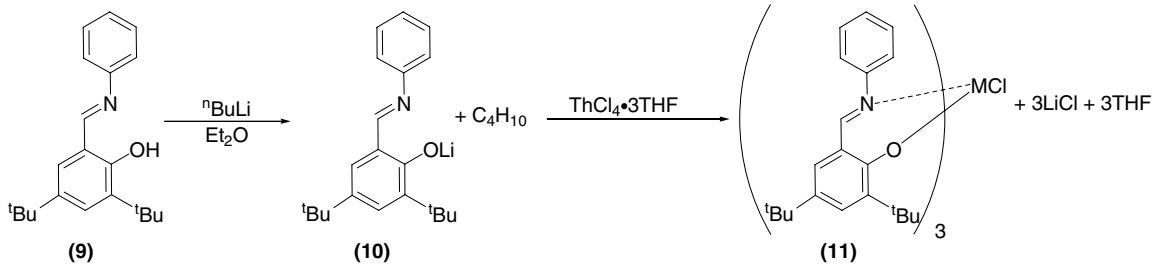


Fig. 2. ORTEP view of $(L)_3ThCl$ (**11**). (Ellipsoids are presented at 50% probability.) Methyl groups of the ^{t}Bu moiety were omitted for clarity.



Scheme 2. Synthesis route for thorium salicylaldiminato complex (**11**).

In addition, we have synthesized and characterized a thorium salicylaldiminato complex, L_3ThCl (**11**), in order to study the effect of the bridging of the ligands on the molecular structure of the complexes. The difference in structure and ligation among the different complexes will entail us to tailor new organic chemical transformations. Preliminary results using these complexes show that they are better catalyst for the coupling of terminal alkynes and isonitriles [16]. A thorough study of these complexes in new catalytic processes is underway and will be presented shortly (see Table 2).

3. Experimental

3.1. Instrumentation

All manipulations were performed on a high vacuum (10^{-5} torr) line, or in a nitrogen filled vacuum atmospheres glovebox with a medium capacity recirculator (1–2 ppm O_2). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. CCl_4 was distilled from P_2O_5, all other hydrocarbon solvents, toluene-d_8 and THF-d_8 (Cambridge Isotopes) were distilled under nitrogen from Na/K alloy.

NMR spectra were recorded on Avance 500 or 300 spectrometer. Chemical shifts for 1H NMR and 13C NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane.

3.2. Syntheses

3.2.1. Synthesis of $ThCl_4 \cdot 3THF$

ThO_2 (8.2 g, 31 mol) was placed in the center of a quartz tube and heated overnight at 200 °C under constant Ar flush. A Schlenk-flask containing freshly distilled CCl_4 was attached to the system. The temperature was raised to 830 °C and a slow Ar flow was directed through the CCl_4 to the quartz tube for 70 h. $ThCl_4$ accumulated in the cool part of the quartz tube. The reaction was monitored by the consumption of the ThO_2. After the completion of the reaction, the tube was transferred into the glove box, and the white solids carefully transferred to a round bottom flask which was connected to a Schlenk-frit. THF (30 ml) was syringed into the flask to dissolve the $ThCl_4$. The volume of the THF was reduced to 20 ml and hexane (30 ml) was syringed carefully to form two layers. The flask was cooled to −30 °C and pale-yellow needle-like crystals of $ThCl_4 \cdot 3THF$ were formed. The crystals were filtered, washed with hexane and dried in vacuum (14.9 g, 25.2 mmol, 81% yield).

Elemental analysis: calculated: C, 24.4; H, 4.1; Cl, 24.0. Experimental: C, 25.5; H, 4.5; Cl, 22.9.

Table 2
Selected bond lengths (Å) and angles (°) for L_3ThCl (**11**)

Th–O1	2.205
Th–O3	2.234
Th–O5	2.239
Th–N2	2.661
Th–N4	2.667
Th–N6	2.702
Th–Cl1	2.689
O1–Th–N2	68.81
O3–Th–N4	67.72
O5–Th–N6	67.43
O1–Th–Cl1	114.66
O3–Th–Cl1	124.69
O5–Th–Cl1	130.33

3.2.2. Synthesis of $(ONOO)Na_2$ (**3**)

A solution of ligand **1** (2 g, 3.90 mmol) in 10 ml THF was added dropwise to a solution of NaH (0.37 g, 15.6 mmol) in 20 ml THF at −78 °C under nitrogen atmosphere over 10 min. the solution was then stirred at room temperature for 2 h and filtered, the solid was washed three times with cold THF. The filtrate was evaporated under low pressure and a white fluffy solid was obtained (90% yield).

1H NMR (300 MHz, THF-d_8): δ 6.98 (d, $J = 2.4$ Hz, 2H, Ar); 6.77 (d, $J = 2.4$ Hz, 2H, Ar); 4.10 (d, $J = 11.7$ Hz, 2H, benzylic); 3.14 (t, $J = 5.4$ Hz, 2H, CH_2); 2.87 (d, 11.7 Hz, 2H, benzylic); 2.66 (t, $J = 5.4$ Hz, 2H, CH_2); 2.41 (s, 3H, OCH_3); 1.43 (s, 18H), ($C(CH_3)$), 1.21 (s, 18H), ($C(CH_3)$). δ ^{13}C NMR (125 MHz, THF-d_8): δ 168.0, 136.0, 129.0, 126.5 (Ar*C*); 125.7, 122.0 (*C*H); 70.2, 65.4 (CH_2); 56.8 (OCH_3); 55.1 (CH_2); 35.4, 33.6 ($C(CH_3)_3$); 32.0, 29.8 ($C(CH_3)_3$).

3.2.3. Synthesis of $(ONNO)Na_2$ (**4**)

This compound was prepared from the precursor **2** by identical procedure to that employed for compound **3**. A white fluffy solid was obtained (94% yield).

1H NMR (300 MHz, THF-d_8): δ 7.01 (d, $J = 2.7$ Hz, 2H, Ar); 6.79 (d, $J = 2.7$ Hz, 2H, Ar); 4.08 (d, $J = 11$ Hz, 2H, benzylic); 2.89 (d, 11 Hz, 2H, benzylic); 2.58 (t, $J = 4$ Hz, 2H, CH_2); 1.91 (t, $J = 4$ Hz, 2H, CH_2); 1.50 (s, 6H, $N(CH_3)_2$); 1.45 (s, 18H), ($C(CH_3)$), 1.22 (s, 18H), ($C(CH_3)$).^{13}C NMR (125 MHz, THF-d_8): δ 180.3, 136.0, 124.0, 122.5 (Ar*C*); 121.8, 120.2 (*C*H); 66.3, 65.0, 63.2 (CH_2); 55.6 (NCH_3); 38.8, 37.5 ($C(CH_3)_3$); 28.5, 27.7 ($C(CH_3)_3$).

3.2.4. Synthesis of $(ONOO)ThCl_2$ (**5**)

A mixture of $ThCl_4 \cdot 3THF$ (0.22 g, 0.36 mmol) and the di-sodium salt of ligand **3** (0.19 g, 0.35 mmol) were dissolved in 30 ml toluene and stirred at room temperature over night under nitrogen atmosphere. A white precipitate was formed and collected over a sinter glass. The collected solid was dissolved in THF, filtered and washed with cold THF three times. The filtrate was removed under reduced pressure to produce $(ONOO)ThCl_2$ (50% yield). The product was crystallized from toluene/hexane at −30 °C.

^{1}H NMR (300 MHz, THF-d_8): δ 7.27 (d, $J = 2.5$ Hz, 2H, Ar); 6.99 (d, 2.5 Hz, 2H, Ar); 5.59 (br, 2H, benzylic); 3.57 (s, 3H, OCH_3); 3.19 (br, 6H, benzylic); 2.67 (br, 2H,

CH_2); 1.45 (s, 18H), (C(CH_3)), 1.29 (s, 18H), (C(CH_3)).^{13}C NMR (125 MHz, THF-d_8): δ 162.1; 141.0, 136.8, 128.2 (Ar*C*); 127.4, 125.0 (Ar*C*H); 76.3, 66.5 (*C*H_2); 65.6 (O*C*H_3); 54.7 (*C*H_2); 36.4, 35.5 (*C*(CH_3)$_3$); 33.0; 31.6 (C(*C*H_3)$_3$). Elemental analysis: calculated: C, 48.77; H, 6.33; N, 1.72; Cl, 8.72. Experimental: C, 49.00; H, 6.57; N, 1.60; Cl, 9.00.

3.2.5. Synthesis of (ONNO)$ThCl_2$ (**6**)

This complex was prepared from the sodium salt of ligand **4** by identical procedure to that employed for complex **5**. A white solid was obtained (47% yield).

^{1}H NMR (300 MHz, THF-d_8): δ 7.28 (d, $J = 2.4$ Hz, 2H, Ar); 6.97 (d, $J = 2.4$ Hz, 2H, Ar); 5.38 (br, 2H, benzylic); 3.58 (br, 2H, benzylic); 3.22 (br, 2H, CH_2); 2.63 (br, 2H, CH_2); 2.26 (s, 6H, N(CH_3)$_2$); 1.46 (s, 18H), (C(CH_3)), 1.27 (s, 18H), (C(CH_3)). ^{13}C NMR (125 MHz, THF-d_8): δ 163.3; 141.0; 131.8; 128.2 (Ar*C*); 127.4, 125.1 (Ar*C*H); 72.4, 69.0, 66.5 (*C*H_2); 65.6 (N*C*H_3); 36.4; 35.5 (*C*(CH$_3$)$_3$); 32.9; 31.6 (C(*C*H_3)$_3$). Elemental analysis: calculated: C, 49.45; H, 6.59; N, 3.39; Cl, 8.59. Experimental: C, 49.51; H, 6.79; N, 3.19; Cl, 8.07.

3.2.6. Synthesis of $(ONOO)_2Th$ (**7**)

$ThCl_4$ (0.27 g, 0.45 mmol) and di-sodium salt of ligand **3** (0.25 g, 0.45 mmol) were mixed together in 30 ml toluene and heated to 70 °C over night. A white precipitate was formed and collected over a sinter glass. The solid was then dissolved with THF and allowed to stand for 2 h till a white solid was precipitated again. The solution was filtered and the solid washed with cold THF three times. The filtrate was then evaporated under reduced pressure and a white solid was obtained (50% yield). The product was crystallized from toluene/hexane at −30 °C.

1H NMR (300 MHz, THF-d_8): 7.24 (m, 4H, Ar); 7.04 (d, $J = 2.4$ Hz, 2H, Ar); 6.97 (d, $J = 2.4$ Hz); 5.72 (d, $J = 13$ Hz, 2H, benzylic); 5.13 (d, $J = 13$ Hz, 2H, benzylic); 3.24 (d, $J = 13$ Hz, 2H, benzylic); 3.22 (d, $J = 13$ Hz, 2H, benzylic); 3.14 (s, 6H, CH_3); 2.95 (t, $J = 4$ Hz, 2H, CH_2); 2.91 (t, $J = 4$ Hz, 2H, CH_2); 2.44 (t, $J = 3$ Hz, 2H, CH_2); 2.39 (t, $J = 3$ Hz, 2H, CH_2); 1.42 (s, 18H), (C(CH_3)), 1.34 (s, 18H), (C(CH_3)); 1.22 (s, 18H), (C(CH_3)); 1.18 (s, 18H), (C(CH_3)). ^{13}C NMR (125 MHz, THF-d_8): δ 163.2, 162.7, 138.9, 138.8, 136.2, 136.1, 128.9, 127.8 (Ar*C*); 127.1, 126.7, 124.8, 124.4 (Ar*C*H); 74.5, 65.9, 64.7 (*C*H_2); 61.8 (O*C*H_3); 49.7 (*C*H_2); 35.8, 35.7, 34.6, 34.5 (*C*(CH$_3$)$_3$), 32.2, 32.1, 31.2, 31.1 (C(*C*H_3)$_3$) Elemental analysis: calculated: C, 63.34; H, 8.21; N, 2.24. Experimental: C, 63.88; H, 7.91; N, 2.03.

3.2.7. Synthesis of $(ONOO)_2U$ (**8**)

UCl_4 (0.14 g, 0.36 mmol) and di-sodium salt of ligand **3** (0.19 g, 0.35 mmol) were mixed together in 30 ml dry toluene and heated to 70 °C over night. The solution was dark green above brown precipitate. The precipitate was collected over a sinter glass and washed with cold toluene three times. The filtrate was removed under reduced pressure and a green solid was obtained (50% yield). The complex was crystallized from toluene at −30 °C.

^{1}H NMR (300 MHz, Toluene d_8): δ 17.5 (br); 12.5 (br); 9.3 (br); 3.41 (s, 2H); 1.28 (s, 18H); −0.20 (s, 18H); −1.25 (s, 2H); −15.1 (br). Elemental analysis: calculated: C, 63.04; H, 8.18; N, 2.23. Experimental: C, 63.58; H, 8.11; N, 2.00.

3.2.8. Synthesis of L_3ThCl (**11**)

1.6 M ^{n}BuLi in hexane (2 ml, 3.20 mmol) was added dropwise over 5 min to a diethylether solution of (3,5-di-*tert*-butylsalicylidene)-aniline (**9**) (1 g, 3.20 mmol) in 20 ml diethylether at −78 °C under argon flow. The mixture was allowed to warm to room temperature and stirred for 12 h. the product was filtered and washed with diethylether over a sinter glass. The filtrate was evaporated under reduced pressure to produce the lithium salt (**10**) as yellow powder (90% yield).

A solution of the lithium salt (0.25 g, 0.79 mmol) in 20 ml diethylether, was added dropwise over 20 min to a solution of $ThCl_4 \cdot 3THF$ (0.238 g, 0.40 mmol) in 20 ml diethylether at −78 °C. The mixture was allowed to warm to room temperature and stirred over night. The mixture was filtered and washed with diethylether. The filtrate was evaporated under reduced pressure to obtain a brown yellow solid. The crude product was dissolved with toluene and filtered, the toluene filtrate was then removed by reduced pressure and replaced with hexane, the solids obtained were washed three times with hexane over a sinter glass to obtain $(Lig)_3ThCl$ as bright yellow solid (50% yield). The complex was crystallized from toluene/hexane at −30 °C.

1H NMR (300 MHz, C_6D_6): δ 8.23 (s, 1H, imine); 7.05–6.79 (m, 7H, Ar); 1.35 (s, 9H, C(CH_3)$_3$); 1.25 (s, 9H, C(CH$_3$)$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 171.7 (Imine *C*H); 163.7, 155.4, 141.4, 140.5, 130.3 (Ar*C*); 128.8, 127.9, 125.6, 122.2, 124.1(Ar*C*H); 36.8, 35.9 (*C*(CH$_3$)$_3$); 31.3, 22.6 (C(*C*H_3)$_3$). Elemental analysis: calculated: C, 63.28; H, 6.83; Cl, 2.96; N, 3.51. Experimental: C, 63.76; H, 6.52; Cl, 2.84; N, 3.35.

3.3. X-ray crystallography

Crystal structure determination: Single crystal immersed in Parathone-N oil was quickly fished with a glass rod and mounted on the KappaCCD diffractometer under a cold stream of nitrogen at 230 K. Data collection was carried out with monochromatized Mo Kα radiation using ω and π scans to cover the Ewald sphere. Accurate cell parameters were obtained with complete collections of intensities and these were corrected in the usual way. The structure was solved by direct methods and completed using successive Fourier difference maps. Refinement was performed anisotropically with respect to the nonhydrogen atoms. Hydrogens were placed at calculated positions and refined using the riding model until convergence was reached (see Table 3).

Table 3
Crystallographic data for complexes **7**, **8** and **11**

Compound	**7**	**8**	**11**
Empirical formula	$C_{66}H_{102}N_2O_6Th$	$C_{66}H_{102}N_2O_6U$	$C_{63}H_{78}ClN_3O_3Th$
Formula weight	1251.54	1257.53	1192.77
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*Cc*	*Cc*	$P2_1/C$
T (K)	230.0(1)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
a (Å)	23.8940(3)	23.729(5)	21.683(4)
b (Å)	17.8770(4)	17.855(4)	13.083(3)
c (Å)	19.0820(3)	18.984(4)	24.143(5)
α (°)	90	90	90
β (°)	127.43	126.97(3)	119.63(3)
γ (°)	90	90	90
V (Å^3)	6472.10(19)	6426(2)	5953(2)
Z	4	4	4
D_{calc} (Mgm^{-3})	1.284	1.300	1.331
Absorption coefficient (mm^{-1})	2.352	2.574	2.594
F(000)	2600	2608	2432
Crystal size (mm)	$0.24 \times 0.21 \times 0.12$	$0.15 \times 0.08 \times 0.04$	$0.35 \times 0.22 \times 0.18$
θ Range for collection (°)	1.57–27.49	1.57–25.35	1.83–25.34
Reflections collected	12199	23711	46043
Unique reflections	12198	5785	10635
R_{int}	0.0254	0.1823	0.0820
Data/restrains/parameter ratio	12198/2/0.6022	5785/17/347	10635/0/60
All R indices	$R_1 = 0.0628$	$R_1 = 0.1115$	$R_1 = 0.0642$
	$wR_2 = 0.0822$	$wR_2 = 0.1258$	$wR_2 = 0.0760$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0392$	$R_1 = 0.0593$	$R_1 = 0.0349$
	$wR_2 = 0.0785$	$wR_2 = 0.1117$	$wR_2 = 0.0696$
Largest difference in peak and hole (e Å^{-3})	0.558 and −0.738	1.126 and −1.362	0.658 and −0.459

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Appendix A. Supplementary material

CCDC 628840, 628844 and 628845 contain the supplementary crystallographic data for **7**, **8** and **11**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.071.

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