Alkyl(aryl)oxy derivatives of thulium(III)

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The reactions of $TmI_2(DME)_3$ with phenol and *tert*-butyl alcohol afforded thulium(III) alkoxyiodides $ROTmI_2(DME)_2$ (R = Ph and Bu^t, respectively). Their structures were determined by X-ray analysis. Monoiodides $(RO)_2TmI(THF)_2$ were synthesized from $TmI_3(THF)_2$ and ROH (taken in a ratio of 1 : 2). Triphenoxides $(RO)_3Tm$ (R = Ph or 2,4,6-$Bu^t_3C_6H_2$) were prepared by the reactions of the naphthalene thulium complex $[C_{10}H_8Tm(DME)]_2C_{10}H_8$ with an excess of the corresponding phenol. The iodide catechoxide complex 3,6-$Bu^t_2C_6H_2O_2TmI(DME)_2$ was prepared by the reaction of $TmI_2(DME)_3$ with 3,6-di-*tert*-butylbenzoquinone-1,2 or 3,6-di-*tert*-butylpyrocatechol.

Key words: thulium(II), thulium(III), phenoxide, alkoxide, iodide, synthesis, structure, reduction.

Recently, it was found that reduction of thulium triiodide with metallic thulium in DME or THF affords the stable molecular complexes of divalent thulium $TmI_2(DME)_3$ (**1**)[1] or $TmI_2(THF)_5$ (**2**)[2], respectively. Attempts to perform an analogous reaction with the participation of $TmBr_3$ or $TmCl_3$ as well as to reduce these salts with sodium failed. However, the extension of the range of Tm^{II} compounds seems to be promising for obtaining new unusually reactive strong reducing agents. Taking into account that complexes **1** and **2** were readily formed from $TmI_3(THF)_2$, we suggested that one of the most probable approaches to the synthesis of these compounds should involve reduction of mixed-ligand Tm^{III} iodides, in particular, alkyl(aryl)oxyiodides. To verify this suggestion, a number of complexes of the $(RO)_2TmI$ and $ROTmI_2$ types as well as triphenoxides $(PhO)_3Tm(DME)$ and $(2,4,6\text{-}Bu^t_3C_6H_2O)_3Tm$ were prepared.

Phenoxide $PhOTmI_2(DME)_2$ (**3**) and *tert*-butoxyiodide $Bu^tOTmI_2(THF)_3$ (**4**) were synthesized by the reactions of compound **1** with phenol in DME and with *tetr*-butyl alcohol in THF, respectively.

$$\underset{\mathbf{1}}{TmI_2(DME)_3} + PhOH \xrightarrow{DME} \underset{\mathbf{3}}{PhOTmI_2(DME)_2} + 1/2\ H_2$$

$$\underset{\mathbf{1}}{TmI_2(DME)_3} + Bu^tOH \xrightarrow{THF} \underset{\mathbf{4}}{Bu^tOTmI_2(THF)_3} + 1/2\ H_2$$

These reactions proceeded readily at room temperature to give the target products in high yields. Sterically hindered phenol 2,4,6-$Bu^t_3C_6H_2OH$ did not react with iodide **1** even upon heating.

Phenoxy derivative **3** was characterized by X-ray analysis. The overall structure of the complex (Fig. 1), which can be described as a seven-coordinate pentagonal bipyramid with halide ligands in the apical positions, is typical of the chemistry of lanthanides. This structural type was observed for the trivalent neutral systems LnX_3L_4, $YCl_3(DME)_2$,[3] $GdCl_3(DME)_2$,[4] $LnCl_3(THF)_4$ (where Ln = Eu[5] or Nd [6]), $SmCl_3(DME)(THF)_2$,[7] and $EuCl_3(py)_4$,[8] for the trivalent cationic complexes $[SmI_2(THF)_5]^+$,[9] $[CeCl_2(THF)_5]^+$,[10] $[TbCl_2(THF)_5]^+$,[11] and $[YCl(OBu^t)(THF)_5]^+$,[12] and for the divalent complexes LnX_2L_5, $TmI_2(DME)_3$,[1] $SmI_2(THF)_5$, $SmI_2(DME)_2(THF)$, and $SmI_2(DME)(THF)_3$.[13] The I(1)—Tm—I(2) angle (176.00(2)°) in molecule **3** is nearly linear. The five donor oxygen atoms are virtually in a single plane (the maximum deviation is 0.27 Å). The O(1) atom deviates from the O(2)—O(5) plane (planar within 0.06 Å) by 1 Å. The dihedral angle between the plane of the phenyl ring of the phenoxide ligand and the plane through the five donor oxygen atoms is 61.2°. The Tm—I bond lengths (3.0021(9) and 3.0236(10) Å) differ from the $TmI_2(DME)_3$ bond lengths (3.141(2) and 3.186(2) Å)[1] by approximately 0.15 Å, which is equal to the difference between the ionic radii of Tm^{II} and Tm^{III}.[14] The Tm—O(DME) bond lengths (2.364(7)—2.444(7) Å) are noticeably smaller than the corresponding distances in the $TmI_2(DME)_3$ molecule. As expected, the Tm—OPh bond (2.025(7) Å) is the shortest contact between the thulium and oxygen atoms in molecule **3**. A direct comparison of this bond length with

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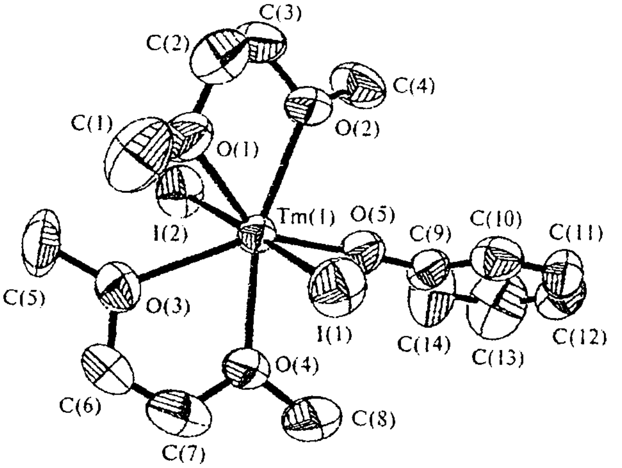


Fig. 1. Molecular structure of complex **3**.

other Ln—OAr distances is impossible because compound **3**, to our knowledge, is the first structurally characterized lanthanide complex with nonsubstituted phenoxide. The terminal position of this ligand is unexpected because all aryl oxides of rare-earth metals, in which the aryl group does not contain bulky substituents at positions 2 and 6, have bridging structures.[15] The Tm—OPh bond length in the molecule of complex **3** is comparable with the Y—O distances (2.046(6) and 2.075(6) Å) in the terminal Y—OAr groups of phenoxide $Y_2(OC_6H_3Me_2\text{-}2,6)_2(THF)_2$.[16]

The complexes containing one iodine atom and two RO groups, *viz.*, $(RO)_2TmI(THF)_x$ (R = Ph, x = 1 (**5**); and R = Bu^t, x = 2 (**6**)), were prepared by the reaction of thulium triiodide with two equivalents of ROK in toluene or THF.

$$TmI_3(THF)_2 + 2\ ROK \longrightarrow \underset{\mathbf{5,\,6}}{(RO)_2TmI(THF)_x} + 2\ KI$$

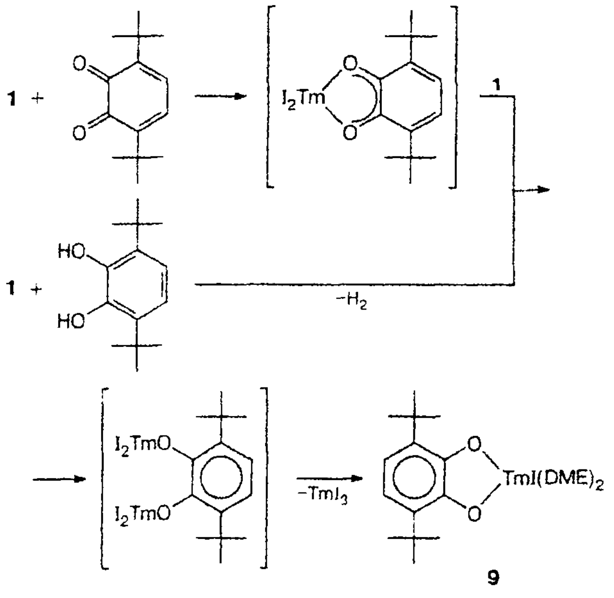
The products were obtained as colorless or pale-yellow powders, which are readily soluble in THF and toluene and insoluble in hexane.

Thulium(III) triphenoxides $(PhO)_3Tm$ (**7**) and $(2,4,6\text{-}Bu^t{}_3C_6H_2O)_3Tm$ (**8**) were synthesized by the reactions of phenols with the naphthalene Tm(III) complex.

$$[C_{10}H_8Tm(DME)]_2C_{10}H_8 + ROH \xrightarrow{DME} \underset{\mathbf{7,\,8}}{(RO)_3Tm} + C_{10}H_{10}$$

The iodide cathecholate thulium(III) complex $3,6\text{-}Bu^t{}_2C_6H_2O_2TmI(DME)_2$ (**9**) was obtained along with TmI_3 in the reaction of compound **1** with 3,6-di-*tert*-butylbenzoquinone-1,2, which proceeded readily in THF or DME at room temperature. Apparently, semiquinolate $(SQ^{\cdot -})TmI_2$, which is formed in the initial stage of this reaction, is reduced with the second TmI_2 molecule to binuclear catecholate $Cat[TmI_2(DME)_n]_2$. The latter undergoes disproportionation to form the observed products. The formation of the same compounds in the reaction of complex **1** with 3,6-di-*tert*-butylpyrocatechol (Scheme 1) is indirect evidence in favor of the suggested scheme. Both reactions afforded pale-yellow-green crystals of **9** (yield >80%).

Scheme 1



Unlike TmI_3, none of the resulting compounds reacted with metallic thulium. In the reactions of complexes **3** and **4** with sodium in THF, the reaction mixture rapidly developed a green color, which is characteristic of Tm^{II} derivatives. However, subsequent gradual removal of the solvent afforded crystals of diiodide **2** rather than the expected oxyiodides $ROTmI(THF)_x$. Reduction in DME also proceeded readily, but crystalline products were not formed. It can be suggested that reduction with sodium in both solvents affords difficultly crystallizable Tm^{II} *at*-complexes $[ROTmI_2(DME)_x][Na(DME)_y]$, which exist in equilibrium with neutral $TmI_2(DME)_3$ and $RONa(DME)_x$. In DME, the complexes exist predominantly in the ionic form, and the removal of the solvent or a decrease in the temperature has no substantial effect on the equilibrium. In THF, concentration of the solution led to shift of the equilibrium to the neutral compounds, one of which was obtained as crystals.

$$ROTmI_2(THF)_3 + Na \xrightarrow{THF} \{[ROTmI_2(THF)_x][Na(THF)_y]\} \rightleftharpoons TmI_2(THF)_5 + NaOR$$

The fact that the RO group rather than iodine is eliminated from the thulium compound agrees with the well-known oxophilicity of alkali metals. However, complexes **5** and **6** containing two RO groups and one I atom, like triphenoxides **7** and **8**, appear to be absolutely inactive with respect to sodium. The green color, which is indicative of reduction of thulium to Tm^{II}, was not observed even upon prolonged stirring of the mixture at 70 °C. After removal of the solvent, the initial compounds were isolated in nearly quantitative yields.

When treated with sodium, semiquinone complex **9** underwent irreversible changes, but derivatives of divalent thulium were not formed. We failed to identify products of this reaction.

Experimental

The syntheses of all compounds, their isolation, and the reactions with sodium were carried out *in vacuo* using the Schlenk technique. The solvents (THF and DME) were dried over sodium benzophenone ketyl and distilled into a reaction tube immediately before use. The IR spectra of the compounds were recorded on a Specord M80 instrument as Nujol mulls. The initial compounds **1** and $[C_{10}H_8Tm(DME)]_2C_{10}H_8$ were synthesized according to known procedures.[1,17]

Complex PhOTmI$_2$(DME)$_2$ (3). Phenol (0.74 g, 7.88 mmol) was added with stirring to a green suspension of compound **1** (2.73 g, 3.94 mmol) in DME (7 mL). The solvent was removed from the resulting colorless mixture by condensation *in vacuo*. The solid residue was washed with cold ether (2×10 mL) to remove an excess of phenol and recrystallized from DME. Compound **3** was obtained in a yield of 2.47 g (90%) as pale-yellow-green (almost colorless) crystals, which decomposed without melting upon heating to >100 °C. Found (%): Tm, 23.90. $C_{12}H_{25}I_2O_5Tm$. Calculated (%): Tm, 24.27. IR, v/cm^{-1}: 870, 1040, 1100, 1160, 1580, 3040.

Complex Bu^{t}OTmI$_2$(THF)$_3$ (4). Complex **4** was prepared from compound **1** (3.58 g, 4.57 mmol) and Bu^{t}OH (1.55 g, 20.95 mmol) under the conditions of the above-described synthesis (but with the use of THF (30 mL) as the solvent) as colorless crystals in a yield of 1.58 g (48.5 %). Found (%): I, 35.36; Tm, 23.64. $C_{16}H_{33}I_2O_4Tm$. Calculated (%): I, 35.67; Tm, 22.37. IR, v/cm^{-1}: 670, 860, 920, 1010, 1200, 1250.

Complex (PhO)$_2$TmI(THF) (5). A mixture of $TmI_3(THF)_2$ (2.56 g, 3.68 mmol), PhOK (0.99 g, 7.49 mmol), and toluene (30 mL) was heated with stirring at 85 °C for 3 h. After centrifugation, the solution was separated from the KI precipitate that formed by decantation and was then filtered from that precipitated. Toluene was removed by condensation *in vacuo*. The residue was dissolved in THF (15 mL) and precipitated with hexane. Compound **5** was obtained as a pale-yellow powder in a yield of 0.99 g (97%). The compound melted with decomposition upon heating to >110 °C. Found (%): Tm, 30.50. $C_{20}H_{26}IO_4Tm$. Calculated (%): Tm, 30.49. IR, v/cm^{-1}: 560, 680, 710, 750, 810, 820, 850, 1000, 1150, 1200, 1290, 1460, 1575.

Complex (Bu^{t}O)$_2$TmI(THF)$_2$ (6). A mixture of $TmI_3(THF)_2$ (1.63 g, 2.35 mmol) and Bu^{t}OK (prepared from *tert*-butyl alcohol (0.35 g, 4.5 mmol) and potassium (0.18 g, 4.7 mmol)) in THF (30 mL) was heated at 70 °C for 8 h. THF was removed by condensation and the solid residue was extracted with toluene (2×20 mL). Toluene was removed from the extract and product **6** was formed as a colorless finely crystalline precipitate. The precipitate was washed with hexane and dried *in vacuo*. Complex **6** was obtained in a yield of 1.09 g (80%). Found (%): I, 21.20; Tm, 29.25. $C_{16}H_{25}IO_4Tm$. Calculated (%): I, 21.67; Tm, 28.84. IR, v/cm^{-1}: 800, 860, 910, 1010, 1190, 1205, 1250.

Complex (PhO)$_3$Tm (7). Phenol (1.88 g, 19.94 mmol) was added with stirring to a suspension of $[C_{10}H_8Tm(DME)]_2C_{10}H_8$ (2.0 g, 4.43 mmol) in DME (20 mL). After 10 min, the precipitate of thulium naphthalene completely dissolved and the solution was decolorized. The solvent was removed by condensation and the solid residue was heated *in vacuo* at 130 °C for 1 h to sublime an excess of phenol and naphthalene liberated. The residue was dissolved in toluene (10 mL) and the product was precipitated with hexane. Compound **7** was obtained in a yield of 1.79 g (90%) as a colorless finely crystalline powder, which decomposed without melting upon heating to >250 °C. Found (%): Tm, 37.00. $C_{18}H_{15}O_3Tm$. Calculated (%): Tm, 37.71. IR, v/cm^{-1}: 575, 690, 705, 845, 885, 1005, 1030, 1080, 1185, 1230, 1485, 1595.

Complex (2,4,6-Bu$^t{}_3$C$_6$H$_2$O)$_3$Tm (8). Compound **8**, which was prepared from $[C_{10}H_8Tm(DME)]_2C_{10}H_8$ (3.1 g, 3.43 mmol) and 2,4,6-tri(*tert*-butyl)phenol (5.45 g, 20.76 mmol) in DME (40 mL) using the same procedure as in the synthesis of **7**, was dissolved (after removal of the solvent and sublimation of volatile compounds *in vacuo* at 200 °C) in hexane at 70 °C. Subsequent cooling of the solution to room temperature afforded compound **8** as pale-yellow-green crystals in a yield of 2.23 g (68%), m.p. 227 °C, μ_{eff} = 8.2 μ_B. Found (%): Tm, 17.14. $C_{54}H_{87}O_3Tm$. Calculated (%): Tm, 17.66. IR, v/cm^{-1}: 530, 640, 715, 755, 815, 850, 885, 895, 925, 1020, 1120, 1235, 1265, 1300, 1350, 1385, 1415, 1460.

Complex 3,6-Bu$^t{}_2$C$_6$H$_2$O$_2$TmI(DME)$_2$ (9). A solution of 3,6-di-*tert*-butylbenzoquinone-1,2 (0.36 g, 1.63 mmol) in DME (15 mL) was gradually added to a suspension of compound **1** (2.4 g, 3.46 mmol) in DME (30 mL). The reaction mixture rapidly turned pale-yellow and a colorless precipitate of $TmI_3(DME)_3$ was formed. The precipitate was filtered off and the solution was concentrated, the solvent being removed by condensation at 60 °C. Slow cooling of the resulting solution to room temperature was accompanied by the formation of virtually colorless crystals of compound **9** in a yield of 0.95 g (85%), m.p. 175 °C, μ_{eff} = 7.4 μ_B. Found (%): Tm, 17.14. $C_{54}H_{87}O_3Tm$. Calculated (%): Tm, 17.66. IR, v/cm^{-1}: 520, 645, 675, 715, 780, 800, 860, 915, 940, 985, 1010, 1050, 1095, 11150, 1235, 1280, 1345, 1375, 1400.

Complex **9** was also prepared from compound **1** (1.7 g, 2.45 mmol) and 3,6-di-*tert*-butylpyrocatechol (0.25 g,

Table 1. Details of X-ray structural study and crystallographic characteristics of complex **3**

Parameter	X-ray conditions and data
Molecular formula	$C_{14}H_{25}I_2O_5Tm$
a/Å	11.2606(10)
b/Å	10.2538(8)
c/Å	19.026(2)
β/deg	99.722(9)
V/Å^3	2165.3(4)
Z	4
Space group	*P*2(1)/*c*
M	696.07
d_{calc}/g cm^{-3}	2.135
Diffractometer	Siemens P4
T/K	293
Radiation	Mo-Kα
Scanning technique	2θ/ω
Number of reflections	5233
σ(*I*)	3
R	0.0506
R_w	0.1213

Table 2. Atomic coordinates of nonhydrogen atoms (×10^4) and equivalent isotropic thermal parameters (U_{eq}×10^3) in complex **3**

Atom	x	y	z	U_{eq}/Å^2
Tm(1)	7408.8 (4)	1361.3(4)	3518.8(2)	49.6(2)
I(1)	4766.2(7)	1221.2(8)	3633.5(5)	80.8(3)
I(2)	10016.7(7)	1312.1(8)	3361.6(5)	82.1(3)
O(1)	6555(7)	817(8)	2294 (4)	73(2)
O(2)	7363(7)	3153(7)	2720(4)	70(2)
O(3)	7683 (8)	−983(7)	3375(4)	83(2)
O(4)	7660(8)	194(7)	4605(4)	75(2)
O(5)	7625(8)	2869(7)	4216(4)	76(2)
C(1)	5674(13)	−206(15)	2081(7)	112(5)
C(2)	6374(15)	1836(15)	1793(7)	106(5)
C(3)	7312(13)	2843(13)	1992(6)	88(4)
C(4)	7985(12)	4359(11)	2894(7)	89(4)
C(5)	8224(15)	−1600(13)	2808(8)	112(5)
C(6)	7971(19)	−1720(13)	4044(9)	128(6)
C(7)	7454(19)	−1173(13)	4588(8)	120(6)
C(8)	7398(17)	713(15)	5269(7)	122(6)
C(9)	7650(10)	3837(9)	4689(5)	61(3)
C(10)	6672(12)	4630(11)	4689(6)	76(3)
C(11)	6672(12)	5610(12)	5170(7)	86(4)
C(12)	7617(15)	5889(13)	5634(7)	87(4)
C(13)	8632(16)	5166(18)	5675(9)	127(6)
C(14)	8639(12)	4123(15)	5188(8)	107(5)

Table 3. Bond lengths (d) and bond angles (ω) in molecule **3**

Bond	d/Å	Angle	ω/deg
Tm(1)—O(5)	2.025(7)	O(4)—Tm(1)—O(2)	159.4(3)
Tm(1)—O(2)	2.379(6)	O(5)—Tm(1)—O(3)	145.1(3)
Tm(1)—O(3)	2.444(7)	O(2)—Tm(1)—O(3)	132.6(3)
Tm(1)—I(1)	3.0236(10)	O(5)—Tm(1)—I(2)	93.8(2)
Tm(1)—O(4)	2.364(7)	O(2)—Tm(1)—I(2)	82.3(2)
Tm(1)—O(1)	2.430(7)	O(3)—Tm(1)—I(2)	80.1(2)
Tm(1)—I(2)	3.0021(9)	O(4)—Tm(1)—I(1)	83.5(2)
O(4)—C(8)	1.446(14)	O(1)—Tm(1)—I(1)	79.8(2)
O(1)—C(2)	1.41(2)	I(2)—Tm(1)—I(1)	176.00(2)
O(2)—C(3)	1.413(13)	O(5)—Tm(1)—O(2)	79.4(3)
O(3)—C(6)	1.47(2)	O(5)—Tm(1)—O(1)	142.0(3)
O(4)—C(7)	1.42 (2)	O(2)—Tm(1)—O(1)	66.6(3)
O(5)—C(9)	1.336(11)	O(4)—Tm(1)—O(3)	66.5(3)
C(6)—C(7)	1.39(2)	O(1)—Tm(1)—O(3)	72.8(3)
C(9)—C(14)	1.37(2)	O(4)—Tm(1)—I(2)	96.0(2)
C(11)—C(12)	1.30(2)	O(1)—Tm(1)—I(2)	97.8(2)
C(13)—C(14)	1.42(2)	O(5)—Tm(1)—I(1)	90.0(2)
		C(9)—O(5)—Tm(1)	173.9(7)

1.23 mmol) in DME (30 mL) under the conditions of the above-described synthesis in a yield of 0.58 g (74%).

X-ray structural study of complex 3. The details of X-ray structural study and the selected crystal-chemical parameters of the single crystal of compound **3** are given in Table 1. A green crystal with dimensions of 0.50×0.40×0.33 mm was placed into a glass capillary. The symmetry group, the crystal class, and the unit cell parameters were determined according to a standard procedure.[18] The data were processed according to a private version of the CARESS program,[19] which employs a modified Leman—Larsen's algorithm for obtaining intensities and standard deviations. All calculations were performed with the use of the SHELXL program package.[20] The structure was solved by the direct method and refined by the full-matrix least-squares method based on F^2. The hydrogen atoms were included in the refinement using the riding model. The atomic coordinates are given in Table 2. The bond lengths and bond angles are listed in Table 3.

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