154 *Russian Chemical Bulletin, International Edition, Vol. 52, No. 1, pp. 154—159, January, 2003*

Reduction of 2,5-di-*tert*-butylcyclopentadienone and pyridine with thulium diiodide. Structures of the complexes $\mathbf{TmI_2(THF)_2[\eta^5\text{-}Bu^t{}_2C_5H_2O]TmI_2(THF)_3}$ and $\mathbf{[TmI_2(C_5H_5N)_4]_2(\mu_2\text{-}N_2C_{10}H_{10})}$

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Reduction of 2,5-di-*tert*-butylcyclopentadienone with two equivalents of thulium diiodide in tetrahydrofuran afforded the binuclear thulium(III) complex with the cyclopentadienyl oxide ligand, *viz.*, $TmI_2(THF)_2[\eta^5\text{-}Bu^t{}_2C_5H_2O]TmI_2(THF)_3$ (**1**). Shielding of the carbonyl carbon atom with two *tert*-butyl substituents prevents pinacolization of the ketyl radical anions that formed upon one-electron reduction of cyclopentadienone. The reaction of thulium diiodide with an excess of pyridine in tetrahydrofuran gave a product of reductive coupling of two pyridine radical anions, *viz.*, $[TmI_2(C_5H_5N)_4]_2(\mu_2\text{-}N_2C_{10}H_{10})$ (**2**). The structures of complexes **1** and **2** were established by single-crystal X-ray diffraction analysis.

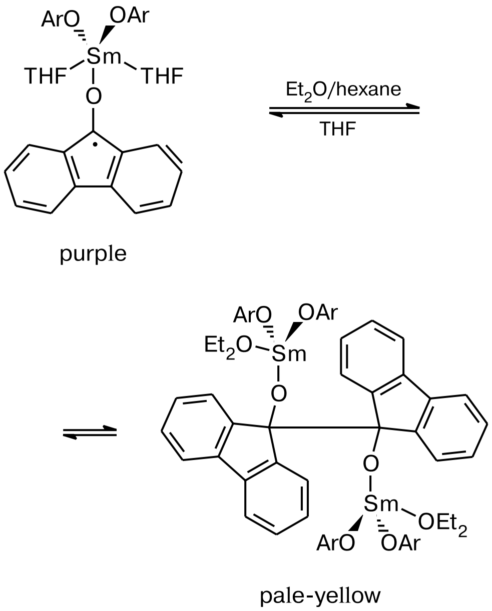
Key words: thulium, reduction, cyclopentadienone, pyridine.

Samarium diiodide SmI_2 finds wide use in organic synthesis as a one-electron reducing agent.[1] Due to its chemical properties, this compound can be used in radical cyclization, addition of ketyl to olefins, pinacolization, nucleophilic acyl substitution, the Barbier, Tishchenko, and Reformatsky reactions, *etc.*[1] Recent studies demonstrated that thulium diiodide TmI_2 [2] is a stronger reducing agent than SmI_2 and has certain advantages over the latter compound. For example, TmI_2 ensures the reaction of 2-phenylethyl chloride with cyclohexanone under mild conditions, whereas SmI_2 is inert toward these reagents even on heating in hexamethylphosphoramide.[4] The study of the reactions of TmI_2 with cyclic conjugated hydrocarbons[3] demonstrated that the reduction potential of TmI_2 in THF is approximately −2.0 V.

Taking into account that the use of TmI_2 in organic synthesis shows promise, it was of considerable interest to reveal the characteristic features of its reactions with various organic substrates. In the present study, we report on the thulium(III) complexes formed by the reactions of thulium diiodide with 2,5-di-*tert*-butylcyclopentadienone and pyridine.

The detailed investigation[5] of the reactions of samarium(II) and ytterbium(II) with fluorenone showed that stability and reactivity of lanthanide complexes with

Scheme 1



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Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 145—150, January, 2003.

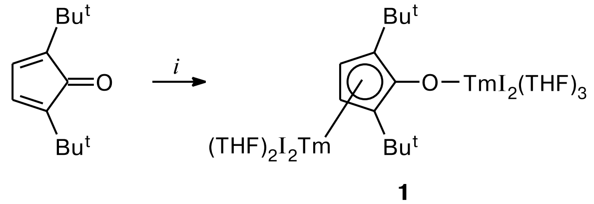
fluorenone ketyl are to a large degree determined by the coordination environment of the metal atom. The bulky ligands (for example, C_5Me_5) in combination with the coordinated THF or HMFA molecules facilitate stabilization of the ketyl radical anion in complexes (Scheme 1). In the case of less bulky ligands or in the absence of THF or HMFA, the ketyl radical anions are dimerized to form a pinacolate structure. In a medium of coordinating solvents, the reverse process, *viz.*, the cleavage of the C—C bond in diol to give ketyl derivatives, takes place.

We suggested that the use of excess thulium diiodide in the reactions with cyclopentadienones would lead to reduction of the cyclopentadienyl radical in the initially formed alkoxide to the cyclopentadienyl anion giving rise to a binuclear product. To suppress dimerization of the ketyl radicals in the reaction, we used cyclopentadienone containing the bulky *tert*-butyl substituents 2,5-$Bu^t_2C_4H_2CO$.

Results and Discussion

Reaction of thulium diiodide with 2,5-di-*tert*-butylcyclopentadienone. Reduction of 2,5-di-*tert*-butylcyclopentadienone with two equivalents of thulium diiodide afforded the binuclear thulium(III) complex $TmI_2(THF)_2(\eta^5$-2,5-$Bu^t_2C_5H_2O)TmI_2(THF)_3$ (**1**) (Scheme 2). The reaction proceeded at room temperature with a rate at which the reagents were mixed, as evidenced by a change in the color of the solution from emerald-green (typical of TmI_2) to orange. Compound **1** was isolated from the reaction mixture as orange crystals, which are poorly soluble in THF and insoluble in ether, DME, and aromatic hydrocarbons. The narrow band of the C=O carbonyl group at 1720 cm^{-1} is the most intense absorption band in the IR spectrum of the starting cyclopentadienone. This band is completely absent from the spectrum of compound **1**. Low-intensity bands at 1750 and 1590 cm^{-1} corresponding to C=C stretching vibrations of cyclopentadienone are also absent from the latter spectrum. The bands of the coordinated THF molecules at 1000 and 830 (850 sh) cm^{-1} are most intense in the spectrum of compound **1**. These bands correspond to C—O stretching vibrations. The medium-intensity bands in the region of 800—700 cm^{-1} belong to H—C(Cp ring) stretching vibrations.

Scheme 2



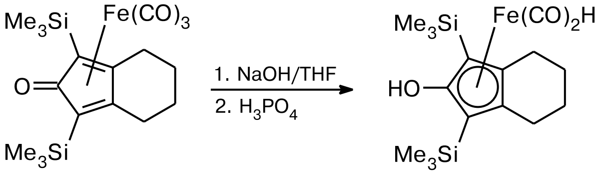
1

orange

i. 2 equiv. of TmI_2, THF

Because of the poor quality of the crystals of complex **1**, which were either obtained directly in the reaction or prepared by recrystallization of compound **1** from THF, X-ray diffraction data were of rather low accuracy. Nevertheless, these data provide a complete view of the molecular structure of the product (Fig. 1). Complex **1** contains two TmI_2 fragments linked through the bridging cyclopentadienyloxy ligand. One of the Tm atoms is η^5-coordinated to the substituted cyclopentadienyl ring (C_5 ring), whereas the second Tm atom is bound to the oxygen atom. The coordination environment about the Tm(1) atom is a distorted tetragonal pyramid with the C_5 ring located in the vertex of the tetragonal pyramid and the O(2), O(3), I(1), and I(2) atoms lying in its base. Only two metal complexes with the η^5-coordinated cyclopentadienyloxy ligand (Ru [6a], Fe [6b]) were synthesized and structurally characterized. Thus, the reaction of an aqueous solution of NaOH with the iron cyclopentadienone complex led to protonation of both the oxygen atom of cyclopentadienone and the iron atom and reduction of the cyclopentadienyl radical to the anion[6b] (Scheme 3).

Scheme 3



yellow

Unlike the Tm(1) atom, the Tm(2) atom in compound **1** has a distorted octahedral environment. Two oxygen atoms, *viz.*, O(1) and O(5), occupy the axial positions of the octahedron; the O(1)—Tm(2)—O(5) angle is 175.5°. The pairs of the I(3) and I(4) atoms (I(4)—Tm(2)—I(3), 162.2°) and the O(4) and O(6) atoms (O(4)—Tm(2)—O(6), 161.8°) are in the equatorial plane of the octahedron in *trans* positions with respect to each other. The thulium—iodine distances in both metal fragments (Tm(1)—I(1), 2.980 Å; Tm(1)—I(2), 2.960 Å; Tm(2)—I(4), 2.945 Å; Tm(2)—I(3), 2.998 Å) are substantially shorter than the corresponding distances in divalent thulium complexes (3.14 and 3.18 Å in $TmI_2(DME)_3$ [2a] and 3.15 Å in $TmI_2(DME)_3(THF)$ [2b]) and are close to the distances typical of thulium(III) derivatives.[7,9]

Apparently, substantial distortions of the coordination spheres about the metal atoms in both groups are associated with the influence of the bulky *tert*-butyl substituents in the C_5 ring and Coulomb repulsions between the metal fragments. It should be noted that all structurally characterized monocyclopentadienyl compounds of

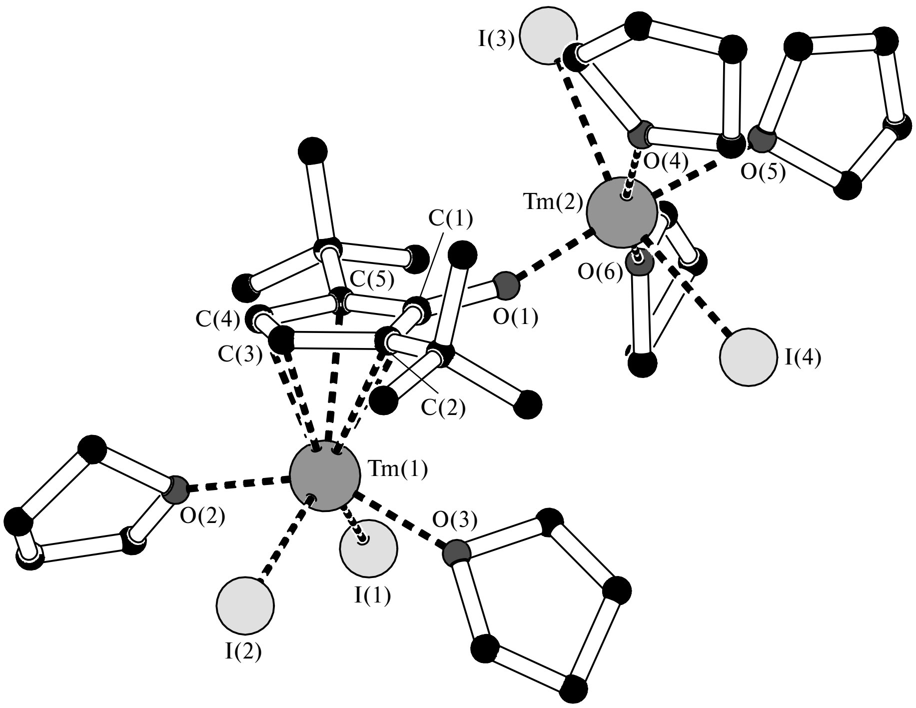


Fig. 1. Molecular structure of the $TmI_2(THF)_2(\eta^5\text{-}Bu^t{}_2C_5H_2O)TmI_2(THF)_3$ complex (**1**). Selected bond lengths (*d*) and bond angles (ω)

Bond	*d*/Å
Tm(1)—O(2)	2.31(3)
Tm(1)—O(3)	2.26(2)
Tm(1)—I(1)	2.980(3)
Tm(1)—I(2)	2.960(3)
Tm(1)—C(1)	2.80(3)
Tm(1)—C(2)	2.73(4)
Tm(1)—C(3)	2.53(4)
Tm(1)—C(4)	2.51(4)

Bond	*d*/Å
Tm(1)—C(5)	2.60(3)
Tm(2)—O(1)	2.06(2)
Tm(2)—O(4)	2.28(2)
Tm(2)—O(5)	2.39(2)
Tm(2)—O(6)	2.33(2)
Tm(2)—I(4)	2.945(4)
Tm(2)—I(3)	2.998(3)
O(1)—C(1)	1.37(4)

Angle	ω/deg
O(3)—Tm(1)—O(2)	143.8(9)
I(2)—Tm(1)—I(1)	117.07(9)
O(1)—Tm(2)—O(4)	100.4(9)
O(1)—Tm(2)—O(6)	97.6(9)
O(4)—Tm(2)—O(6)	161.8(8)
O(1)—Tm(2)—O(5)	175.5(8)
I(4)—Tm(2)—I(3)	162.17(9)
C(1)—O(1)—Tm(2)	164(2)

the late lanthanides $CpLnX_2$ (X = Cl, Br, or CF_3OSO_3), unlike the $TmI_2(THF)_2(Bu^t{}_2C_5H_2O)$ fragment, contain three coordinated tetrahydrofuran molecules, *i.e.*, they are described by the formula $CpLnX_2(THF)_3$ and have octahedral structures. The $OTmI_2(THF)_3$ fragment also has an octahedral structure untypical of the $LnX_3(L)_n$ complexes (X is a halogen atom or another η^1-coordinated anion). The seven-coordinate pentagonal-bipyramidal coordination with the halide ligands in the apical positions is typical of the $LnX_3(L)_n$ systems.[8] As an example, we refer to the thulium complex $(PhO)TmI_2(DME)_2$ containing the η^1-coordinated phenoxy group (isoelectronic to the cyclopentadienyloxy anion in complex **1**).[9]

A detailed analysis of the geometry of the cyclopentadienyl ring presented difficulties because of high thermal vibrations of the carbon atoms. However, the η^5-coordination of the Tm(1) atom by this ligand is beyond question. The distances between the Tm(1) atom and five carbon atoms of the ring, although varying over a wide range (2.51—2.80 Å), do fall in the range observed in other thulium(III) cyclopentadienyl complexes.[7,10] It should be noted that the Tm(1) atom is slightly shifted from the center of the C_5 ring toward the C(3) and C(4) atoms devoid of substituents. The Tm(1)—C(3) and Tm(1)—C(4) distances (2.53 and 2.51 Å, respectively) are noticeably shorter than the Tm(1)—C(1), Tm(1)—C(2), and Tm(1)—C(5) distances (2.80(3), 2.73, and 2.60 Å, respectively). Apparently, this shift is associated with steric hindrances caused by the *tert*-butyl substituents and the second thulium-containing fragment.

The Tm(2)—O(1) distance (2.06 Å) is close to the Tm—OPh distances in the $PhOTmI_2(DME)_2$ complex[9] (2.025 Å) and the calix-4-arene derivative of thulium(III), *viz.*, (5,11,17,23-tetra-*tert*-butyl-25,27-dioxo-26,28-dimethoxy[4]-arene)thulium iodide,[11] (2.035 Å). The O(1)—C(1) distance (1.37 Å) is also close to the O—Ph distances in the phenoxy[9] and calixarene[11] derivatives (1.334 and 1.330 Å, respectively). In most of the known lanthanide complexes with the heterobidentate cyclopentadienylalkoxy ligands, the alkoxide group is in the β position with respect to the cyclopentadienyl ring.[12] In the series of lanthanide derivatives of this type, complex **1** is the first representative in which the oxygen atom of the $OLnI_2$ group is bound directly to the carbon atom of the cyclopentadienyl ring.

Reaction of thulium diiodide with pyridine. In the earlier study,[13] dark-blue products were obtained upon the addition of pyridine to a solution of TmI_2 in dimethoxyethane. However, attempts to isolate and identify these products were unsuccessful. Our attempts to achieve more success in this reaction with the use of the same solvent by varying the reagent ratio also failed. Nevertheless, we found that the reaction in THF proceeded differently. This allowed us to isolate a product that formed in the initial step of the reaction.

Upon the addition of pyridine to a green solution of TmI_2 in THF at the temperature from −10 to 0 °C, the reaction mixture immediately turned red. After concentration of the reaction mixture *in vacuo*, dark-red crystals of the $[TmI_2(C_5H_5N)_4]_2(\mu_2\text{-}N_2C_{10}H_{10})$ complex (**2**) (Fig. 2) precipitated. The IR spectrum of compound **2** has a large set of absorption bands among which are the bands corresponding to C=N stretching vibrations (1630, 1595, and 1575 cm^{-1}) and very intense absorption bands of the C—H bonds (arom.) in the region of 610—760 cm^{-1}. The magnetic moment of the complex at room temperature (6.05 μ_B) is somewhat smaller than the values typical of Tm^{III} (7.0—7.5 μ_B)[14] and differs substantially from μ_{eff} of Tm^{II} (4.5 μ_B),[2] which indicates that the metal atom was oxidized to the trivalent state in the course of the reaction. The observed decrease in the magnetic moment of product **2** might be associated with the exchange interaction between two thulium atoms belonging to the same molecule. It should be noted that an analogous decrease in μ_{eff} has been observed earlier[15] in the binuclear thulium complex $[(\eta^2\text{-}C_{10}H_8)Tm]_2(\eta^4\text{-}C_{10}H_8)$ containing the bridging naphthalene dianion.

Compound **2** crystallized from THF in the tetragonal space group $P4_2/mbc$ with four molecules per unit cell. Each molecule contains four chemically and crystallographically equivalent fragments (see Fig. 2). As can be seen from Fig. 2, the reaction of TmI_2 with pyridine is accompanied by reductive coupling of pyridine molecules. Earlier, analogous dimerization of acridine has been observed[16] in the reaction with $(C_5Me_5)_2Sm$. Recently, it has been reported[17] that benzene underwent dimerization under the action of potassium metal in the presence of 18-crown-6. In complex **2**, the coordination environment about the thulium atom is a distorted pentagonal bipyramid, as evidenced by the I—Tm—I bond angle (171.4°). Two iodine atoms are in *trans* positions and occupy vertices of the pentagonal bipyramid. Five nitrogen atoms involved in the environment about the metal atom are located in the equatorial plane. As ex-

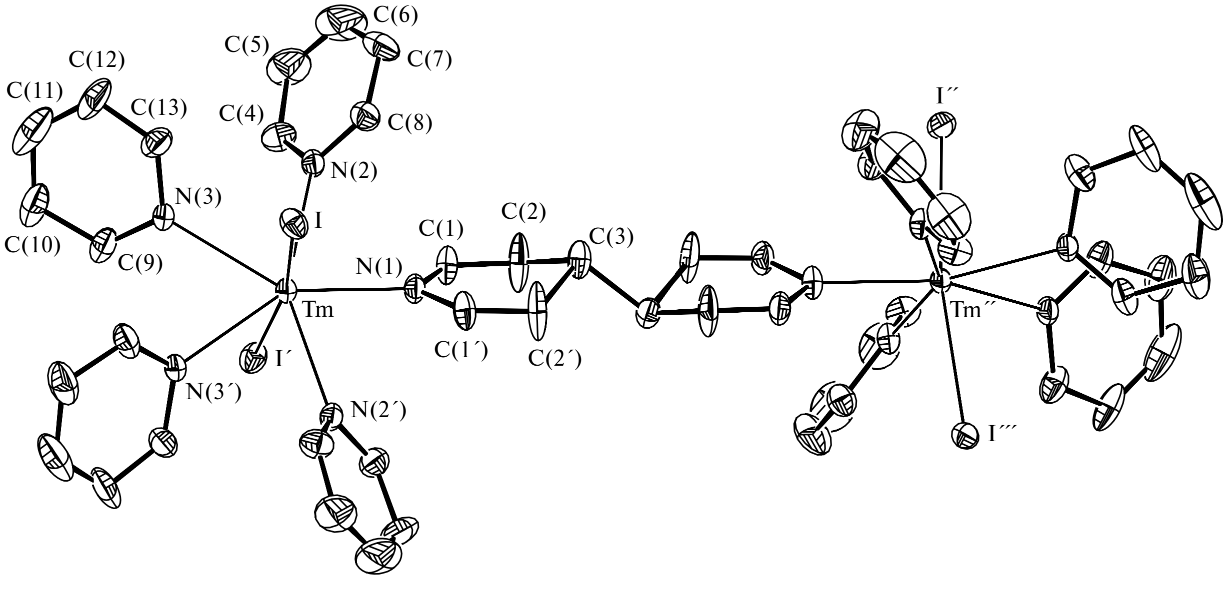


Fig. 2. Molecular structure of $[TmI_2(C_5H_5N)_4]_2(\mu_2\text{-}N_2C_{10}H_{10})$ complex (**2**). Selected bond lengths (*d*) and bond angles (ω).

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Tm—I	2.9948(9)	Tm—N(2)	2.499(10)	N(1)—Tm—N(2)	75.1(2)	N(1)—Tm—I	94.30(2)
Tm—N(1)	2.301(14)	Tm—N(3)	2.550(10)	N(2)—Tm—N(3)	70.0(3)	I—Tm—I	171.40(4)
				N(3)—Tm—N(3′)	69.9(5)		

pected, the Tm—I distances in **2** (2.99 Å) are shorter than the corresponding Tm—I distances (aver. 3.16 Å) in $TmI_2(DME)_3$ [2] and are close to the Tm—I distances in $[TmI_2(HMPA)_4][I](py)_5$ (3.0452 Å),[13] $[TmI(HMPA)_4(py)][I]_2$ (3.0057 Å),[13] (η^8-C_8H_8)TmI(THF)$_2$ (3.0338 Å),[3] and (η^5:η^5-$C_{24}H_{16}$)TmI(THF) (2.9227 Å).[3] The distances between the thulium atom and the nitrogen atoms of the coordinated pyridine molecules (2.49 and 2.55 Å) are much longer than that between the thulium atom and the nitrogen atom of the bridging dipyridyl fragment (2.30 Å), which can be considered as a bis-amide ligand. Its geometry cannot be analyzed rigorously because of the large thermal parameters of the carbon atoms of this ligand.

Experimental

All operations were carried out either *in vacuo* or in an atmosphere of dry nitrogen using the Schlenk technique. Tetrahydrofuran was dried and stored over sodium benzophenone ketyl and distilled *in vacuo* immediately before use. Thulium diiodide $TmI_2(THF)_x$ was prepared *in situ* according to a known procedure.[3] The IR spectra were recorded on a Specord M-80 instrument. Samples were prepared under an atmosphere of dry argon as Nujol mulls. The percentage of lanthanide in the complexes was determined by titration with Trilon B (Xylenol Orange). The magnetic susceptibility was measured by the relative method using Moore's salt as the standard on an apparatus developed[18] in the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences.

Pentakis(tetrahydrofuran)(μ_2-η^5:η^1-2,5-di-*tert*-butylcyclopentadienyloxy)bis(thulium diiodide) (1). A solution of 2,5-di-*tert*-butylcyclopentadienone (0.375 g, 1.95 mmol) in THF was added with vigorous stirring to a solution of thulium diiodide, which was prepared *in situ* from iodine (1.0 g, 3.93 mmol) and an excess of thulium, in THF (35 mL). The reaction mixture immediately turned orange. The solution was immediately filtered. After one day, orange crystals of compound **1** (2.08 g, 76%) precipitated from the solution at ~20 °C, m.p. 127 °C (decomp.). Found (%): Tm, 24.74. $C_{33}H_{60}I_4O_6Tm_2$. Calculated (%): Tm, 24.17. IR (Nujol mulls), ν/cm^{-1}: 1395 m, 1295 w, 1215 m, 1040 w, 1000 s, 910 w, 825 v.s (850 sh), 780 m, 745 m, 665 s.

Bis[tetrakis(pyridine)thulium diiodide]-1,1´-dihydro-4,4´-bipyridyl (2). Pyridine (4.97 g, 62.83 mmol) was added to a suspension of thulium diiodide (prepared from iodine (1.02 g,

Table 1. Crystallographic data for complexes **1** and **2**

Parameter	**1**	**2**
Molecular formula	$C_{33}H_{60}I_4O_6Tm_2$	$C_{50}H_{50}I_4N_{10}Tm_2 \cdot 2\ C_4H_8O$
Molecular weight		
Crystal dimensions/mm^3	0.30×0.18×0.12	0.38×0.20×0.18
Crystal system	Orthorhombic	Tetragonal
Space group	$Pna2_1$	$P4_2/mbc$
Unit cell parameters		
a/Å	17.5099(3)	19.2826(3)
b/Å	14.5427(3)	19.2826(3)
c/Å	17.0258(2)	23.4713(4)
$\alpha = \beta = \gamma$/deg	90.0	90.0
V/Å^3	4335.47(13)	8727.1(2)
Z	4	4
ρ_{calc}/g cm^{-3}	2.142	1.355
μ/mm^{-1}	6.950	3.469
F(000)	2624	3400
$2\theta_{max}$/deg	48	55
Ranges of indices of measured reflections	$-20 \le h \le 19$ $-16 \le k \le 16$ $-19 \le l \le 14$	$-25 \le h \le 25$ $-17 \le k \le 25$ $-30 \le l \le 30$
Number of measured reflections	23814	60716
Number of independent reflections	5884	5141
(R_{int})	(0.1296)	(0.1355)
Number of reflections with $I > 2\sigma$	5884	5141
Number of parameters in the refinement	218	175
GOOF(F^2)	1.157	1.512
R_1* (based on F for reflections with $I > 2\sigma(I)$)	0.0997	0.0810
wR_2** (for all reflections)	0.2257	0.2176
Residual electron density/e • Å^{-3}, ρ_{min}/ρ_{max}	−3.474/3.325	−1.152/2.416

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ** $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

4.02 mmol) and an excess of thulium) in THF (45 mL) *in vacuo* on cooling to the temperature from −10 to 0 °C. The color of the reaction mixture changed from green to red. The solution was concentrated *in vacuo* to 25 mL. Crystallization at 0 °C afforded compound **2**$\cdot$2 C_4H_8O as red crystals in a yield of 1.89 g (53%), m.p. >57 °C (decomp.). Found (%): Tm, 19.49. $C_{50}H_{50}I_4N_{10}Tm_2\cdot 2\ C_4H_8O$ (1780.71). Calculated (%): Tm, 18.97. IR (Nujol mulls), ν/cm^{-1}: 1630 s, 1595 s, 1570 s, 1485 m, 1430 s, 1375 m, 1280 s, 1205 s, 1155 w, 1075 v.s, 1050 m, 1005 m, 980 s, 905 s, 855 s, 760 m, 730 m, 700 v.s, 610 s, 590 s. μ_{eff} = 6.02 μB.

X-ray diffraction study of complexes 1 and 2. The X-ray diffraction data for both complexes were collected on a Siemens SMART CCD diffractometer (ω scan technique, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator) at 173 K. The absorption corrections were applied with the use of the SADABS program[19] (transmission (max/min) was 0.551705/0.265642 and 0.636845/0.445277 for **1** and **2**, respectively). The structures were solved by direct methods with the use of the SHELXS97 program package[20] and refined by the full-matrix least-squares method based on F^2 with the use of the SHELXL97 program package.[21] In the structure of compound **1**, only the Tm and I atoms were refined anisotropically. For compound **2**, all nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions (U_{iso} = 0.08 Å^3). The geometric parameters of the structures of complexes **1** and **2** were analyzed with the use of the PLATON program.[22] The crystallographic data, details of X-ray diffraction study, and characteristics of the refinement of complexes **1** and **2** are given in Table 1. The complete tables of atomic coordinates and thermal parameters were deposited with the Cambridge Structural Database.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 01-03-32631) and the Alexander von Humboldt Foundation (Alexander von Humboldt Stiftung).

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Received April 29, 2002;
in revised form August 29, 2002