Lanthanide Complexes
with 1,4,7-Trimethyl-1,4,7-triazacyclononane

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Abstract—The reaction of 1,4,7-trimethyl-1,4,7-triazacyclononane with samarium, gadolinium, and terbium chloride tetrahydrofuranates gives mononuclear complexes $[LnCl_3(Me_3tacn)(THF)_n]$ (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane; Ln = Sm (**I**), Gd (**II**), $n = 1$; Ln = Tb (**III**), $n = 0$). The treatment of complexes **I** or **II** with 1,2,4-triphenylcyclopentadienyl potassium affords mono(cyclopentadienyl) complexes $[Cp^{Ph3}LnCl_2(Me_3tacn)]$ (Cp^{Ph3} = 1,2,4-triphenylcyclopentadienyl; Ln = Sm (**IV**), Gd (**V**)). Complexes **IV** and **V** are formed even when a twofold excess of $Cp^{Ph3}K$ is used. The molecular structure of complexes **I**–**V** was established by X-ray diffraction analysis (CCDC nos. 2299485 (**I**), 2299487 (**II**), 2299486 (**III**), 2305352 (**IV**), 2306051 (**V**)).

Key words: lanthanides, 1,4,7-trimethyl-1,4,7-triazacyclononane, cyclopentadiene, X-ray diffraction analysis

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INTRODUCTION

The coordination and organometallic compounds of lanthanides have attracted increasing attention of researchers in recent years; therefore, preparation of accessible precursors for the synthesis of these compounds is an important task [1]. The most widely used precursors are anhydrous lanthanide chlorides $LnCl_3$ or their tetrahydrofuran adducts $LnCl_3(THF)_x$ with a variable content of THF (THF = tetrahydrofuran). However, poor solubility of these compounds in most organic solvents restricts their use. Therefore, many researchers made attempts to prepare mononuclear halide complexes of lanthanides, yttrium, and scandium with well-defined composition and structure such as $[MCl_3(L)_n]$, where L is a ligand, a donor of electron pair, coordinated to the Ln^{3+} ion. Among other complexes, $[LnCl_3(DME)_2]_n$, $[LnCl_3(triethylene\ glycol)_n]$, $[LnCl_3(THF)_2(tmeda)]$, and $[LnCl_3(Py)_4]$ (DME = 1,2-dimethoxyethane, tmeda = tetramethylethylenediamine, Py = pyridine) have been obtained [2–6]. Such adducts of rare earth metal chlorides are readily soluble in organic solvents, since the introduction of polydentate ligands into the

coordination sphere prevents the formation of less soluble polynuclear complexes.

We assumed that the use of tridentate N-donor ligand, 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn) may result in the formation of mononuclear complexes like $[LnCl_3(Me_3tacn)(THF)_n]$ with an enhanced solubility in organic solvents compared to $LnCl_3$ and $LnCl_3(THF)_x$.

There are a number of organometallic compounds ($[Cp^{Ph3}LnCl_2(Me_3tacn)]$ (Ln = Nd, Tb [7]), $[CpNd(BH_4)_2(Me_3tacn)]$ [8], and $[Ln(Alkyl)_{3-n}Cl_n(Me_3tacn)]$ (Ln = La, Y, Sc [9–13])) and coordination compounds ($[MI_3(Me_3tacn)(THF)]$ (M = La, U [14, 15]), $[LnHal_3(Me_3tacn)]$ (Ln = Y, Sc [9, 14, 16, 17])) of trivalent f-elements with 1,4,7-trimethyl-1,4,7-triazacyclononane. All structurally characterized complexes are mononuclear, except for the oxygen-bridged binuclear complex $[\{YI_2(Me_3tacn)\}_2(\mu\text{-}O)]$ [17]. The studies of Me_3tacn complexes were mainly concentrated on lanthanum, yttrium, and scandium derivatives, whereas examples of lanthanide complexes with 4f elements of the middle of the series are scarce.

The goal of the present work is to synthesize and study the structure of samarium, gadolinium, and terbium halide complexes with trimethyltriazacyclononane and to evaluate the applicability of these compounds as synthetic precursors of cyclopentadienyl lanthanide complexes.

EXPERIMENTAL

Compounds **I–V** were synthesized in the atmosphere of purified argon in anhydrous solvents using a SPECS-GB2 glovebox. Tetrahydrofuran was pre-dried over NaOH and distilled from potassium/benzophenone. Hexane was distilled from sodium–potassium eutectic/benzophenone. Tetrahydrofuran-d_8 was stored over sodium–potassium alloy in an evacuated ampoule. The $LnCl_3(THF)_3$ complexes (Ln = Sm, Gd, Tb) [18] were prepared by known procedures. The compound $Cp^{Ph3}H$ (Cp^{Ph3} = 1,2,4-triphenylcyclopentadienyl) [19] was recrystallized from absolute ethanol and dried in vacuo. Potassium hydride (30 wt % dispersion in mineral oil) was washed with anhydrous hexane and dried in vacuo. Hexamethyldisilazane (99.9%, Fujifilm) was distilled under argon and degassed. KHMDS (HMDS = hexamethyldisilazide) was obtained from KH and hexamethyldisilazane in toluene. 1,4,7-Trimethyl-1,4,7-triazacyclononane was synthesized by a known procedure [20], dried over anhydrous sodium sulfate, and degassed in vacuo. NMR spectra were recorded on a Bruker AVANCE III HD instrument (400 MHz). Elemental analysis of complexes **I–V** was carried out on a PerkinElmer 2400 Series II elemental CHNS/O analyzer. The metal content was determined by complexometric titration with EDTA using the xylenol orange indicator. The content of chloride ions was determined by potentiometric titration with a standard silver nitrate solution.

Synthesis of [SmCl₃(Me₃tacn)(THF)] (I). A solution of Me₃tacn (0.034 g, 0.2 mmol) in THF (4 mL) was added with stirring to a suspension of SmCl₃(THF)₄ (0.098 g, 0.18 mmol) in THF (10 mL). The reaction mixture was stirred for 12 h. The solution was separated from the precipitate by centrifugation (4000 rpm, 7 min) and the precipitate was washed with THF (5 mL). Hexane (20 mL) was carefully added to the combined solutions, so as to avoid mixing of the layers. After 3 days, colorless crystals were formed. The crystals were dried under dynamic vacuum. The yield of the colorless crystals of **I** was 0.044 g (0.088 mmol, 49%).

¹H NMR (THF-d_8; δ, ppm): 0.96 s (9H, CH_3), 3.56 (6H, CH_2), 4.46 m (6H, CH_2). ¹³C{¹H} NMR (THF-d_8; δ, ppm): 49.5 (CH_3), 61.6 (CH_2).

For $C_{13}H_{29}N_3OCl_3Sm$

Anal. calcd., %	C, 31.22	H, 5.85	N, 8.40
Found, %	C, 30.98	H, 5.79	N, 8.24

The crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution of **I** in THF.

The synthesis of [GdCl₃(Me₃tacn)(THF)] (II) was performed by the procedure described above starting from Me₃tacn (0.086 g, 0.5 mmol) and GdCl₃(THF)₃ (0.230 g, 0.48 mmol). The yield of the colorless crystals of **II** was 0.165 g (0.327 mmol, 68%).

For $C_{13}H_{29}N_3OCl_3Gd$

Anal. calcd., %	C, 30.79	H, 5.77	N, 8.29	Cl, 21.01	Gd, 31.04
Found, %	C, 29.35	H, 5.55	N, 8.64	Cl, 21.20	Gd, 30.71

The crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution of **II** in THF. The underestimated carbon content in the elemental analysis data may be due to either partial dissociation of coordinated THF during drying in vacuo or gadolinium carbide formation during elemental analysis. To confirm that the sample integrity is retained after vacuum drying, the metal and chlorine contents of the complex were determined by titration.

The synthesis of [TbCl₃(Me₃tacn)] (III) was performed by the procedure described above starting from Me₃tacn (0.034 g, 0.2 mmol) and TbCl₃(THF)₃ (0.087 g, 0.18 mmol). The yield of the colorless crystals of **III** was 0.051 g (0.117 mmol, 65%).

For $C_9H_{21}N_3Cl_3Tb$

Anal. calcd., %	C, 24.75	H, 4.85	N, 9.63
Found, %	C, 25.02	H, 4.79	N, 9.63

The crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution of **III** in THF.

Synthesis of [Cp^{Ph3}SmCl₂(Me₃tacn)](THF) (IV). A solution of KHMDS (0.040 g, 0.2 mmol) in toluene (1 mL) was added with stirring to a solution of Cp^{Ph3}H (0.059 g, 0.2 mmol)) in toluene (3 mL). The reaction mixture was stirred for 10 min, the precipitated Cp^{Ph3}K was separated by centrifugation (4000 rpm, 4 min), washed with toluene (3 mL), and dissolved in THF (4 mL). A solution of Cp^{Ph3}K was carefully added to a solution of **I** (0.100 g) in THF (6 mL), so as to avoid mixing of the phases. After 2 days, crystals and a dispersed precipitate were formed. The crystals were separated from the precipitate by decantation, washed with THF (5 mL), and dried in a dynamic vacuum. The yield of orange crystals of **IV** was 0.068 g (0.099 mmol, 50%).

For $C_{32}H_{38}N_3Cl_2Sm$

Anal. calcd., %	C, 56.04	H, 5.59	N, 6.13
Found, %	C, 56.21	H, 5.18	N, 6.13

The crystals suitable for X-ray diffraction were obtained by slow diffusion of a $Cp^{Ph3}K$ solution in THF into a solution of **I** in THF. According to X-ray diffraction data, the unit cell of complex **IV** contains one THF molecule. This solvent molecule is lost during vacuum drying.

The synthesis of $[Cp^{Ph3}GdCl_2(Me_3tacn)](THF)$ (V) was performed by the procedure described above starting from KHMDS (0.100 g, 0.5 mmol), $Cp^{Ph3}H$ (0.147 g, 0.5 mmol), and **II** (0.252 g, 0.5 mmol). The yield of the colorless crystals of **V** was 0.150 g (0.216 mmol, 43%).

For $C_{32}H_{38}N_3Cl_2Gd$

Anal. calcd., %	C, 55.48	H, 5.53	N, 6.07
Found, %	C, 54.89	H, 5.46	N, 5.62

The crystals suitable for X-ray diffraction were obtained by slow diffusion of a $Cp^{Ph3}K$ solution in THF into a solution of **II** in THF. According to X-ray diffraction data, the unit cell of complex **V** contains one THF molecule. This solvent molecule is lost during vacuum drying.
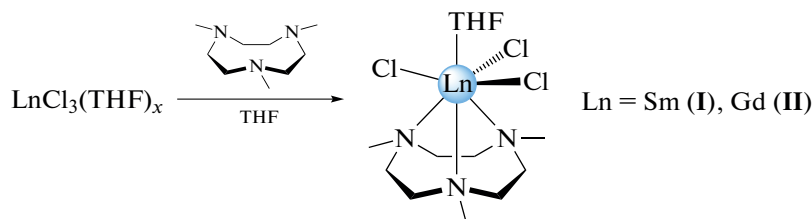
X-ray diffraction analysis of complexes **I**–**IV** was carried out on a Bruker Quest D8 diffractometer (Photon-III detector, MoK_α radiation, ω-scan mode). The reflection intensities were determined using the SAINT program [21]. The absorption corrections were applied semiempirically based on equivalent reflections using the SADABS software [22]. X-ray diffraction study of complex **V** was carried out on a Rigaku Synergy S diffractometer (κ-geometry, HyPix6000HE detector, CuK_α radiation, ω-scan mode). The reflection intensities were obtained and analytically corrected using the CrysAlisPro program [23]. The structures were solved by the direct method using the SHELXT program [24] and refined with the

least-squares methods in the full-matrix anisotropic approximation on F_{hkl}^2 with the SHELXL-2018 software [25]. For refinement of the disordered moieties, constraints for atomic displacement parameters and positional parameters were used (DFIX and EADP). The hydrogen atoms in all structures were calculated using the riding model (C–H distances of 0.980 Å for methyl and 0.990 Å for methylene hydrogen atoms) and refined in the relative isotropic approximation $U_{iso}(H) = 1.2U_{equiv}(C)$. The main crystallographic data and refinement parameters for compounds **I**–**V** are summarized in Table 1.

The atom coordinates and other parameters of the structures of **I**–**V** were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2299485–2299487, 2305352, 2306051, deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The treatment of suspensions of samarium and gadolinium chloride tetrahydrofuranates in THF with a solution of 1,4,7-trimethyl-1,4,7-triazacyclononane leads to fast dissolution of $LnCl_3(THF)_x$ precipitates to give colorless solutions of $[LnCl_3(Me_3tacn)(THF)]$ (Ln = Sm (**I**), Gd (**II**); Scheme 1). The addition of hexane to the resulting solutions results in the formation of complexes **I** and **II** as colorless crystals. Complexes **I** and **II** are formed even when the reaction is carried out with three equivalents of Me$_3$tacn. Both compounds are moderately soluble in THF and pyridine, but are insoluble in hydrocarbon solvents, whereas the related $[LaI_3(Me_3tacn)(THF)]$ complex is moderately soluble in toluene [14]. For samarium and gadolinium, complexes of this type were unknown previously.

Scheme 1. Synthesis of complexes **I** and **II**.

The structures of the obtained compounds were established by X-ray diffraction. The samarium and gadolinium complexes are isostructural and crystallize in the space group $P2_1/n$. The lanthanide atoms are coordinated by three nitrogen atoms of Me$_3$tacn, three chloride ligands, and the THF oxygen atom; the coordination numbers are 7 (Fig. 1). According to calculations by the SHAPE program, version 2.1, the coordination polyhedra of samarium and gadolinium [26]

are best described as monocapped octahedra with approximate C_{3v} symmetry. The shape measures indicating the deviation of the metal coordination polyhedra from the ideal monocapped octahedron are 0.759 and 0.684 for **I** and **II**, respectively (when the shape measure is zero, the metal coordination polyhedron corresponds to the reference polyhedron, while a value less than unity reflects a slight distortion of the polyhedron [26]). If we assume that Me$_3$tacn occupies one

Table 1. Main crystallographic data and refinement details for compounds **I**–**V**

Parameter	Value				
	I	**II**	**III**	**IV**	**V**
Molecular formula	$C_{13}H_{29}N_3OCl_3Sm$	$C_{13}H_{29}N_3OCl_3Gd$	$C_9H_{21}N_3Cl_3Tb$	$C_{32}H_{38}N_3Cl_2Sm$, C_4H_8O	$C_{32}H_{38}N_3Cl_2Gd$, C_4H_8O
M	500.09	506.99	436.56	758.01	764.91
T, K	120(2)	120(2)	100(2)	100(2)	100.0(1)
Radiation wavelength, Å	0.71073	0.71073	0.71073	0.71073	1.54184
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$
$Z(Z')$	4 (1)	4 (1)	4 (1)	4 (1)	4 (1)
a, Å	9.7572(3)	9.7763(12)	12.6526(7)	13.7403(7)	13.7240(1)
b, Å	14.9777(5)	14.9323(17)	7.6238(4)	15.3557(9)	15.3412(1)
c, Å	12.6648(4)	12.6683(18)	15.8926(9)	15.9646(9)	16.0315(1)
β, deg	91.2293(10)	91.226(4)	90.481(2)	101.431(2)	101.477(1)
V, Å^3	1850.41(10)	1848.9(4)	1532.96(15)	3301.6(3)	3307.82(4)
ρ(calcd.), g cm^{-3}	1.795	1.821	1.892	1.525	1.536
μ, mm^{-1}	3.608	4.022	5.117	1.974	14.701
$F(000)$	996	1004	848	1548	1556
$2\theta_{max}$, deg (completeness)	58 (0.999)	59 (1.000)	62 (0.996)	59 (0.998)	136 (1.000)
Number of measured reflections	18385	18229	68955	32791	48724
Number of unique reflections	4913	4920	5535	9196	6039
Number of reflections with $I > 2\sigma(I)$	3975	3787	4432	7087	5875
Number of refined parameters	197	197	162	384	426
R_1 ($I > 2\sigma(I)$)	0.0317	0.0373	0.0465	0.0501	0.0729
wR_2 (all data)	0.0681	0.0783	0.1212	0.1184	0.1805
GOOF	1.058	1.011	1.139	1.037	1.075
Residual electron density (min/max), e Å^{-3}	−1.302/0.623	−1.324/1.038	−2.685/1.911	−1.096/2.129	−1.106/3.893

site in the coordination sphere, the coordination polyhedron of each Ln^{3+} ion is a distorted trigonal bipyramid. The Ln−N bond lengths are in rather narrow ranges, 2.604(3)−2.650(3) and 2.588(3)−2.624(3) Å for **I** and **II**, respectively (Table 2).

The ^1H NMR spectrum of the samarium complex (**I**) exhibits three signals: a singlet for methyl group protons and two signals for non-equivalent protons of methylene groups, indicating that C_3-symmetry of the complex is retained in solution and that the complex is structurally rigid. The non-equivalence of the protons of ethylidene CH_2 groups attests to the rigid structure of the coordinated 9-membered ring, which is obviously caused by strong binding of the ligand to the metal, which is retained even in a THF solution (Fig. 2).

The reaction of Me_3tacn with terbium chloride tetrahydrofuranate $TbCl_3(THF)_3$ in THF results in the formation of the $[TbCl_3(Me_3tacn)]$ complex (**III**) (Scheme 2). Compound **III** was isolated in a pure state by recrystallization from a 1 : 1 THF−hexane mixture. Complex **III** is moderately soluble in THF and pyridine, but is insoluble in hydrocarbon solvents.
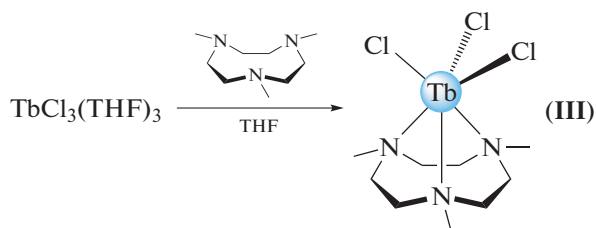
Scheme 2. Synthesis of complex **III**.

The structure of complex **III** was established by X-ray diffraction. Complex **III** is isostructural to the previously described yttrium $[YCl_3(Me_3tacn)]$ and scandium $[ScCl_3(Me_3tacn)]$, $[ScF_2Cl(Me_3tacn)]$ complexes [16, 17]. The $\{TbCl_3\}$ moiety is disordered over two positions, with the occupancies ratio being
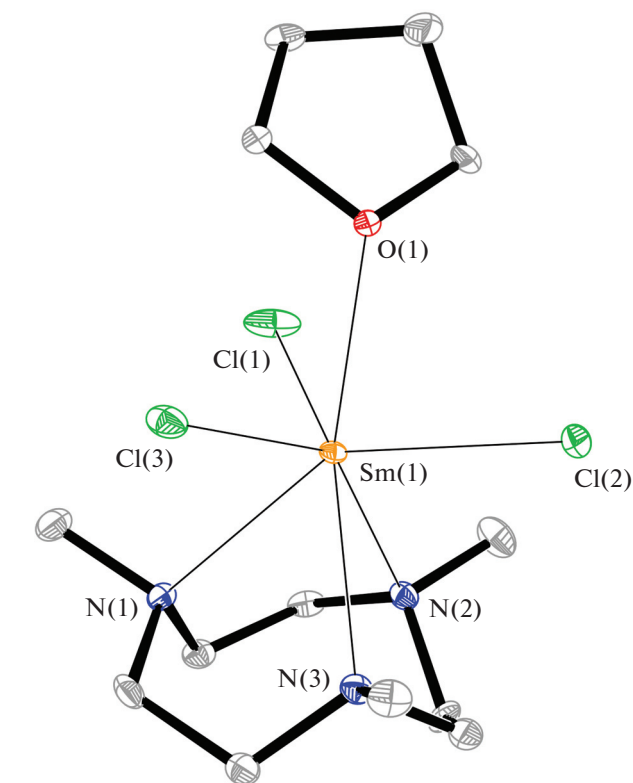

Fig. 1. Molecular structure of complex **I** with atoms represented by thermal ellipsoids ($\rho = 50\%$). The hydrogen atoms and disorder of the coordinated THF molecule are omitted for clarity.

96 : 4. The terbium atom in **III** is coordinated by three chloride ligands and three nitrogen atoms of Me_3tacn, with the coordination number being 6 (Fig. 3). The $Tb-Me_3tacn_{centroid}$ distance is 1.882 Å, which is shorter than the analogous distance in $[Cp^{Ph3}TbCl_2\text{-}(Me_3tacn)]$ (1.990 Å) [7], but is in line with that dis-

Table 2. Main structural parameters of complexes **I**−**V***

Parameter	I	II	III	IV	V
Ln−N bond lengths, Å	2.604(3)−2.650(3)	2.588(3)−2.624(3)	2.500(6)−2.530(5)	2.599(3)−2.690(3)	2.589(4)−2.677(5)
Ln−Me$_3$tacn$_{centroid}$ distances, Å	2.031	2.000	1.882	2.032	2.013
Difference between the Ln−Me$_3$tacn$_{centroid}$ distance and Ln^{3+} ionic radius, Å	1.011	1.000	0.959	0.953	0.960
Ln−Cl bond lengths, Å	2.6496(9)−2.6580(9)	2.621(1)−2.634(1)	2.571(2)−2.580(2)	2.618(1), 2.643(1)	2.595(1), 2.627(1)
Ln−O$_{THF}$ bond lengths, Å	2.559(2)	2.551(3)			
Ln−(ClClCl) distance, Å	0.683	0.681	1.144		

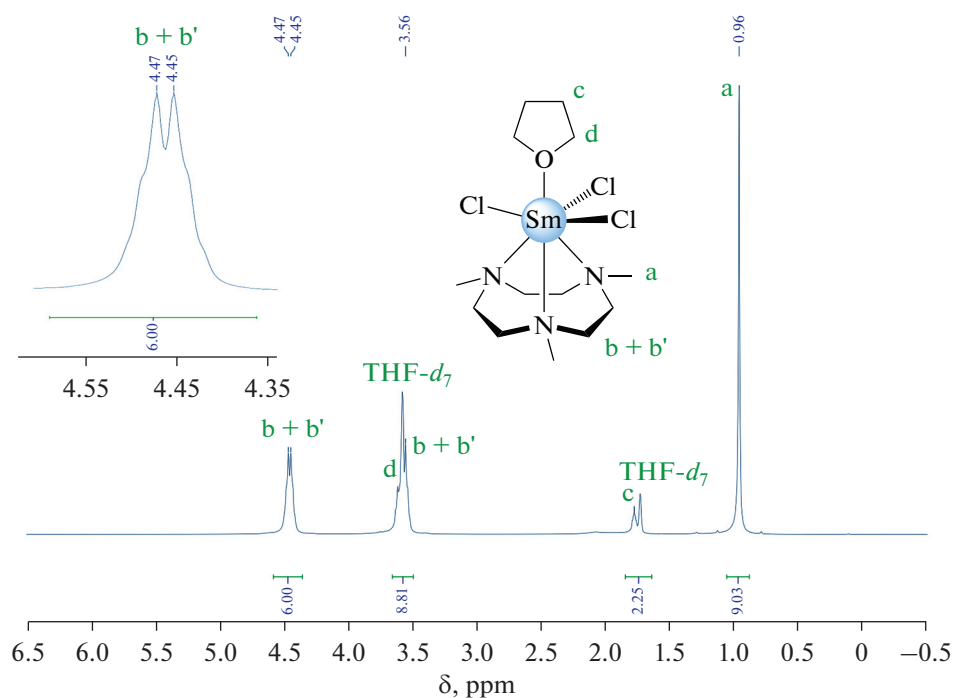* For complex **III**, structural parameters of the moiety with higher occupancy are given.

Fig. 2. ^{1}H NMR spectrum of complex **I**. The inset shows an enlarged fragment of the spectrum with the signal at 4.46 ppm.

tance considering the decrease in the coordination number. The differences between the Tb–Me$_3$tacn$_{centroid}$ distances and the Tb^{3+} ionic radii for C.N. of 6 and 8 are 0.959 and 0.950 Å for **III** and [Cp^{Ph3}TbCl$_2$(Me$_3$tacn)], respectively. According to calculations by the SHAPE

program, version 2.1, the terbium coordination polyhedron is best described as a distorted octahedron (the shape measure is 2.027 for the moiety with higher occupancy [26]).

Complex **III** differs from the above complexes **I** and **II** by the absence of THF coordinated to the metal, which is, most likely, due to the smaller radius of the Tb^{3+} ion compared to the Sm^{3+} and Gd^{3+} ions.

We suggested that complexes **I**−**III** can be used as the starting reactants for the synthesis of organometallic lanthanide derivatives. Previously, complexes like [LnCl$_3$(Me$_3$tacn)] were used only to obtain lanthanide alkyl derivatives [9, 12, 16]. As compared with the widely used lanthanide chloride tetrahydrofuranates LnCl$_3$(THF)$_x$, complexes **I**−**III** possess two considerable advantages, that is, well-defined structure and better solubility in organic solvents. The possibility of this application was demonstrated by the synthesis of mono(cyclopentadienyl) complexes from these compounds. Treatment of complexes **I** and **II** in tetrahydrofuran with one equivalent of 1,2,4-triphenylcyclopentadienyl potassium Cp^{Ph3}K affords the mono(cyclopentadienyl) complexes [Cp^{Ph3}LnCl$_2$-(Me$_3$tacn)] (Ln = Sm (**IV**), Gd (**V**); Scheme 3). Complexes **IV** and **V** have an exceptionally poor solubility in THF and are insoluble in other organic solvents.
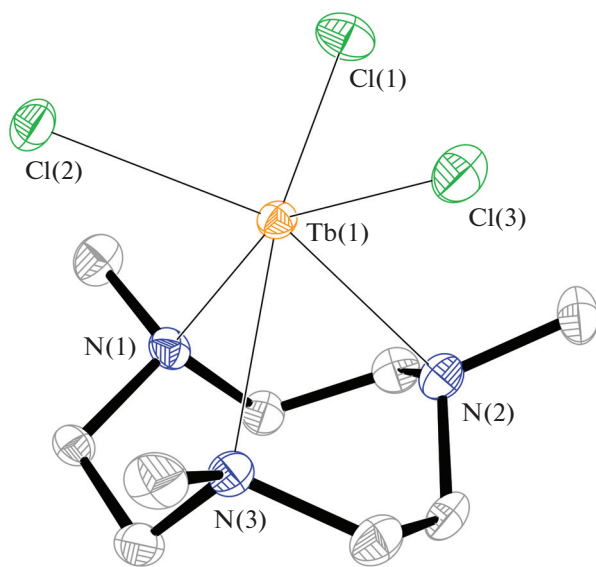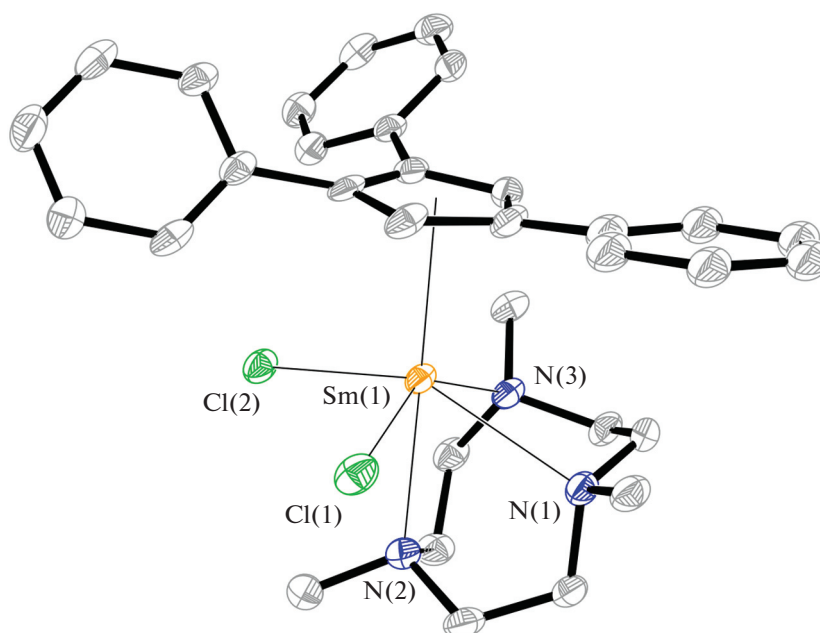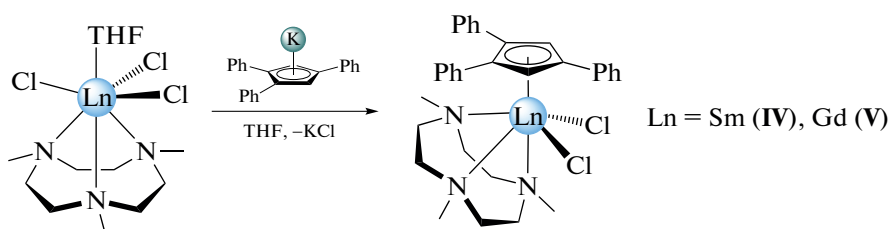

Fig. 3. Molecular structure of complex **III** with atoms represented by thermal ellipsoids (ρ = 50%). The hydrogen atoms and disorder of the {TbCl$_3$} moiety are omitted.

Fig. 4. Molecular structure of complex **IV** with atoms represented by thermal ellipsoids (ρ = 50%). The hydrogen atoms, the THF molecule, and disorder of one of the phenyl substituents are omitted.

Scheme 3. Synthesis of complexes **IV** and **V**.

The use of two equivalents of $Cp^{Ph3}K$ in reactions with **I** and **II** also affords mono(cyclopentadienyl) complexes, while bis(cyclopentadienyl) derivatives are not formed. Note that in the case of related uranium complex $[UI_3(Me_3tach)_2]$, containing a more labile six-membered heterocycle, 1,3,5-trimethyl-1,3,5-triazacyclohexane, the replacement of halide ligands by cyclopentadienyl groups does not stop after the formation of mono(cyclopentadienyl) derivatives, but proceeds until tris(cyclopentadienyl) complexes are formed [15].

The possibility of preparing mono(cyclopentadienyl) complexes like **IV** and **V** from lanthanide mono(cyclopentadienyl) dichloride ate-complexes and trimethyltriazacyclononane was demonstrated in our previous study in relation to neodymium and terbium complexes [7].

The structures of complexes **IV** and **V** were determined by X-ray diffraction (Fig. 4); they are isostructural to the neodymium and terbium complexes we described earlier [7]. The Sm–Cp$_{centroid}$ distance is 2.556 Å; it is markedly longer than analogous dis-

tances in other samarium mono(cyclopentadienyl) complexes (e.g., it is 2.451 Å in $[CpSmBr_2(THF)_3]$ [27], 2.463 Å in $[(C_9H_7)SmI_2(THF)_3]$ [28], and 2.452 Å in $[(Me_5C_5)SmI_2(THF)_3]$ [29]); this is apparently attributable to the effective Sm–Me_3tacn interaction. A more correct comparison can be made for the gadolinium complex, in which the Gd–Cp$_{centroid}$ distance is 2.546 Å, whereas in the related mono(triphenylcyclopentadienyl) complex $[\{Cp^{Ph3}GdCl_2(THF)\}_2KCl(THF)]_2$, the Gd–Cp$_{centroid}$ distances for two crystallographically non-equivalent gadolinium atoms are 2.444 and 2.458 Å [30].

The rotation angles of the phenyl groups relative to the cyclopentadienyl ring in **IV** and **V** are in the range typical of mono(triphenylcyclopentadienyl) lanthanide complexes [31]; in the samarium complex, these angles are 38.0° and 46.9° for the substituents in positions 1 and 2 of cyclopentadiene and 9.1° and 13.3° for the substituent in position 4 (there are two values because of the disorder). In both complexes, there are short C–H···π contacts between one methyl group of

Me$_3$tacn and *ipso-* and *ortho-*carbon atoms of the phenyl substituent in cyclopentadiene position 4 (the H···C distances are in the 2.39–2.50 Å range for **IV** and 2.33–2.52 Å for **V**).

In this study, we obtained and structurally characterized lanthanide chloride complexes with a triazacyclononane ligand. Unlike the complex of terbium, which has a smaller ionic radius, samarium and gadolinium complexes contain THF molecules coordinated to the metal. In relation to samarium complexes, the structural rigidity of triazacyclononane complexes in a THF-d$_8$ solution was demonstrated; in solution, the N-donor ligand is still coordinated to the metal. The applicability of lanthanide triazacyclononane complexes as the starting compounds for the synthesis of cyclopentadienyl derivatives was studied in relation to samarium and gadolinium complexes. The ligand exchange of compounds **I** and **II** with triphenylcyclopentadienyl potassium leads to mono(cyclopentadienyl) complexes **IV** and **V**. The use of excess Cp^{Ph3}K does not lead to the formation of bis(cyclopentadienyl) products. The effective Ln−Me$_3$tacn interaction in **IV** and **V** results in increasing Ln−Cp$_{centroid}$ distances compared to those in analogous lanthanide mono(cyclopentadienyl) complexes without additional ligands.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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