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Spontaneous Association of the Terbium Cyclopentadienyl Complexes under Controlled Hydrolysis

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Abstract—Controlled hydrolysis of the terbium cyclopentadienyl complexes results in the formation of the heteroligand tetranuclear terbium complex $[\{Tb(\eta^5\text{-}C_5H_5)\}_3\{Tb(THF)_3\}(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_6(\mu_4\text{-}O)]$ (**I**), the recrystallization of which from tetrahydrofuran (THF) gives solvatomorph $\mathbf{I} \cdot 0.5THF$ (**Ia**). According to the X-ray structure analysis data (CIF files CCDC 1569329 (**I**) and 1569330 (**Ia**)), the complexes are tetrahedral with the μ_4-bridging O^{2-} anion at the center of the tetrahedron. The cyclopentadienyl ligand in complex **I** is shown to act as an "antenna" providing luminescence of the complex.

Keywords: rare-earth metals, X-ray structure analysis, luminescence, cyclopentadienyl ligand

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INTRODUCTION

Cyclopentadienyl (Cp) complexes of rare-earth metals predominate in the organometallic chemistry of 4*f* elements from the middle of the 20th century when the first organolanthanide compounds, tris-Cp complexes $[Ln(C_5H_5)_3]$, have been discovered [1, 2]. Their heteroligand analogs, mono- and bis-Cp halide complexes of rare-earth metals $[Ln(C_5H_5)_2Cl]_2$ [3] and $[Ln(C_5H_5)Cl_2(THF)_3]_2$, were synthesized later [4]. In spite of considerable diversity of ligands in the modern chemistry of 4*f* elements, the Cp ligand and its substituted analogs still play the leading role in the organometallic chemistry of rare-earth elements [5, 6].

The development of the chemistry of Cp complexes of rare-earth metals is caused, to a high extent, by the possibility of relatively easy modification of the Cp ligand by the substitution of one or several hydrogen atoms of the five-membered ring. Significant changes in the steric hindrance of the ligand that occur during the substitution make it possible to purposefully change the properties of the organolanthanide ligands, whose reactivity is considerably controlled, as was repeatedly mentioned, by the volume of the ligands and coordination saturation of the complex [7, 8].

One of specific features of the coordination and organometallic compounds of rare-earth metals is spontaneous association to form polynuclear complexes with bridging donor ligands between Ln^{3+} cations. The formation of these polynuclear complexes is due to a tendency of lanthanide to form complexes with a high coordination number of the central ion [9]. The formation of such structures is most characteristic of the complexes with carboxylate and alkoxide ligands [10, 11]. Nevertheless, polynuclear structures can be formed even for the tris-Cp complexes having no donor ligands. A combination of two factors, the steric hindrance of the ligand and the ionic radius of the metal changing with moving along the 4*f* series, leads to a change in the degree of association from the mononuclear $[Ln(C_5H_5)_3]$ (Ln = Yb) to coordination polymers $[Ln(C_5H_5)_3]_\infty$ (Ln = La, Pr, Nd) [6].

In this work, we report the possibility of the purposeful construction of tetranuclear structures of terbium Cp complexes with the Tb_4 tetrahedral framework by the controlled hydrolysis of the terbium Cp complexes.

EXPERIMENTAL

The compounds described are very sensitive to air and moisture. All synthetic procedures were conducted in a glove box (SPECS, Russia) under argon. The solvents used were distilled under argon, tetrahydrofuran (THF) was distilled over potassium/benzophenone, and hexane was distilled over a potassium–sodium alloy. Compounds $TbCl_3(THF)_3$ and C_5H_5Na were obtained using described procedures [12, 13]. Terbium content was determined by direct complexonometric titration with the Xylenol orange indicator.

Synthesis of $[\{Tb(\eta^5\text{-}C_5H_5)\}_3\{Tb(THF)_3\}(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_6(\mu_4\text{-}O)]$ (I). A solution of sodium cyclopentadienyl (0.110 g, 1.25 mmol) in THF (10 mL) was added with stirring to a suspension of $TbCl_3(THF)_3$ (0.482 g, 1 mmol) in THF (20 mL), and stirring was continued for 24 h. A 0.42 M solution (0.61 mL) of H_2O in THF was slowly added dropwise to the obtained reaction mixture with vigorous stirring, and then stirring was continued for 3 days. A precipitate formed was separated by centrifugation. The solution was concentrated to 50% volume, and hexane (50 mL) was added carefully in such a way that the solvents layers would not mix up. In 4 days, a colorless microcrystalline precipitate of complex **I** was formed due to the slow diffusion of hexane to a solution of the complex in THF. The precipitate was decanted from the solution. Solvatomorph **I** · 0.5THF (**Ia**) was formed by the recrystallization of complex **I** from THF.

For $C_{27}H_{39}O_4Cl_7Tb_4$ (**I**)

Anal. calcd., %	C, 24.73	H, 3.00	Tb, 48.47
Found, %	C, 23.10	H, 2.89	Tb, 46.47

Fluorescence and phosphorescence spectra were recorded on a PerkinElmer LS-55 spectrofluorimeter. The Origin 8.6 program package was used for data processing. For the operation with compounds unstable in air, a sealed quartz cell 4 mm in diameter and a sample holder, which makes it possible to exactly centre the cell relative to the optical scheme of the instrument, were specially designed. All measurements were carried out at 300 K.

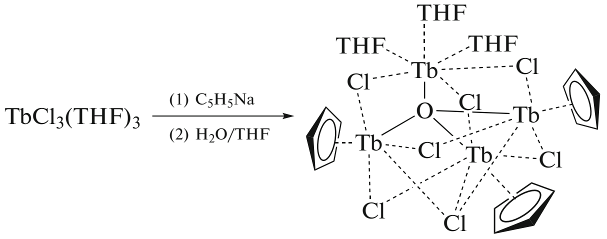
X-ray structure analyses of single crystals of complexes **I** and **Ia** were carried out on a SMART APEX2 CCD diffractometer (MoK_α radiation, graphite monochromator, ω scan mode). The structures were solved by a direct method and refined by least squares in the anisotropic full-matrix approximation for F^2_{hkl}. Restraints were imposed on the positional and thermal parameters when refining disordered THF molecules. The positions of hydrogen atoms were calculated geometrically and refined in the isotropic approximation by the riding model. All calculations were performed using the SHELXTL PLUS program package. The main crystallographic data and refinement parameters for compounds **I** and **Ia** are given in Table 1.

The coordinates of atoms and other parameters of the structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC 1569329 (**I**) and 1569330 (**Ia**); deposit@ccdc. cam. ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Poorly soluble in THF complex **I** was primarily isolated as a by-product of the recrystallization of the bis(cyclopentadienyl) complex $[Tb(\eta^5\text{-}C_5H_5)_2\text{-}Cl(THF)]$ (**II**) from a THF–hexane (1 : 2, vol/vol) mixture. The structure of complex **I** was determined by X-ray structure analysis (Fig. 1, Table 1).

Evidently, complex **I** is formed due to the hydrolysis of the intermediately formed terbium Cp halide complex. To check this assumption, we carried out the target synthesis of compound **I** by the reaction of terbium chloride with the stoichiometric amount of sodium cyclopentadienyl followed by hydrolysis controlled by the amount of water.



This reaction led to the formation of complex **I** as an adduct with THF in a yield of 90%. The recrystallization of complex **I** from THF gives solvatomorph **Ia** containing 0.5 THF molecule. A comparison of two crystal structures shows that the structure of complex **I** in them is the same in fact, except for the mutual arrangement of the THF molecules. Taking into account that complex **Ia** precipitated as very small crystals and the final accuracy of data obtained for it turned out to be low, all other parameters are further presented for compound **I**.

The structure of compound **I** determined by X-ray structure analysis is based on a tetrahedron formed by four terbium cations bound by the μ_4-bridging oxygen atom localized at the center of the tetrahedron. In addition to the $\mu_4\text{-}O^{2-}$ ligand, three of four terbium cations (Tb(1), Tb(2), Tb(3)) are η^5-coordinated by the Cp ligands, three μ_2-bridging chlorine anions, and one μ_3-bridging chlorine anion. The Tb(4) cation is coordinated by three THF molecules, μ_4-bridging oxygen atom, and three μ_2-bridging chlorine anions. The structural motif $Tb_4(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_6(\mu_4\text{-}O)$ has the local symmetry C_{3v}. The coordination number of the Tb cations coordinated by the Cp anion (Tb(1–3)) is 8, and the coordination number of the Tb(4) cation

Table 1. Crystallographic data for complexes **I** and **Ia**

Parameter	Value	
	I	**Ia**
Empirical formula	$C_{27}H_{39}O_4Cl_7Tb_4$	$C_{29}H_{43}O_{4.5}Cl_7Tb_4$
FW	1311.41	1347.46
Temperature of recording, K	120(2)	120(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.3654(6)	11.1328(14)
b, Å	11.9248(6)	12.004(2)
c, Å	15.6918(8)	18.627(2)
α, deg	81.5177(7)	87.225(3)
β, deg	80.9100(7)	76.498(2)
γ, deg	63.0019(7)	62.752(2)
V, Å^3	1864.19(17)	2146.8(5)
Z	2	2
ρ_{calc}, g cm^{-1}	2.336	2.084
μ, cm^{-1}	80.26	69.73
Range of θ, deg	2.26–30.00	2.26–26.500
Number of measured/independent reflections	22368/10799	26526/8855
R_{int}	2.01	5.09
Number of reflections with $I > 2\sigma(I)$	9908	6954
Number of refined parameters	436	384
R_1 with $I > 2\sigma(I)$	2.22	4.33
wR_2 for all reflections	4.64	11.52
GOOF for F^2	1.098	1.056

is 7. This difference is manifested in different Tb–O distances equal to 2.178(2) Å for the Tb(4)–(μ_4-O) bond and 2.333(2)–2.362(2) Å for the remaining Tb–(μ_4-O) bonds.

An analysis of the Cambridge Structural Database System (CSDS) [14] shows that the discrete tetrahedral fragment Ln_4O with the O^{2-} ion at the center of the tetrahedron is rare in the coordination chemistry of rare-earth elements.

There are 106 structures with the Ln_4O fragment in the CSDS, but only 37 of them contain the discrete tetrahedral Ln_4O fragment. Eight of them are attributed to the Cp derivatives of rare-earth metals, and the molecular structures of three of them ([{(η^5-1,2,4-$Ph_3C_5H_2$)Lu}$_3${Lu(THF)$_3$}(μ_3-Cl)(μ_2-Cl)$_6$(μ_4-O)](THF)$_2$ [15], [Er_4(η^5-C_5H_9–C_5H_4)$_3$(μ_3-Cl)(μ_2-Cl)$_6$(μ_4-O)(THF)$_3$] [16], and [(η^5-CH_3–C_5H_4)$_3$-Yb_4(μ_3-Cl)(μ_2-Cl)$_6$(μ_4-O)(THF)$_3$] [17]) are closest to the structure of compound **I**.

It is known that the organic ligands containing the conjugated π-system in the rare-earth metal complexes can play the role of an "antenna" efficiently absorbing electromagnetic radiation and providing more intensive emission in the luminescence of the complex due to the subsequent energy transfer to the rare-earth metal ion. However, the Cp ligand was not almost studied as an "antenna" in complexes of rare-earth metals.

The UV-irradiated sample of complex **Ia** demonstrates luminescence typical of the Tb^{3+} ion and caused by the transitions $^5D_4 \to {}^7F_i$ (I = 6–3; lines at 490, 546, 586, and 620 nm, respectively) (Fig. 2a), and the band corresponding to the $^5D_4 \to {}^7F_5$ transition is most intensive. On going from the fluorescence to phosphorescence spectra (Fig. 2b) (delay from 0.2 to 3.5 ms), the emission spectrum does not change substantially. This indicates that the Tb^{3+} ions are the only emission centers and no luminescence of the organic ligand occurs.

The excitation fluorescence and phosphorescence spectra are similar, but the former contains a distinct maximum at 270 nm corresponding, probably, to the absorption maximum of the Cp ligand. The efficient

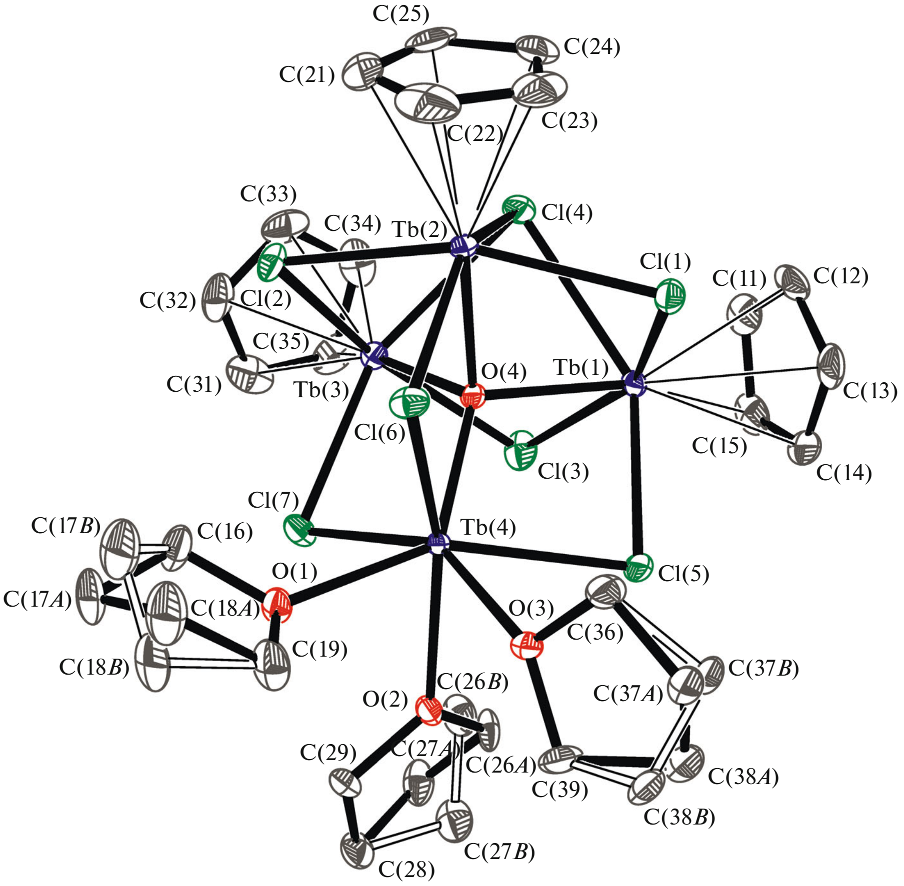


Fig. 1. Molecular structure of compound **I**. Selected bond lengths Tb(1)–O(4) 2.362(2), Tb(2)–O(4) 2.333(2), Tb(3)–O(4) 2.334(2), Tb(4)–O(4) 2.1782(19); Tb(1)–Cl(5) 2.6770(8), Tb(1)–Cl(1) 2.6965(8), Tb(1)–Cl(3) 2.7122(8), Tb(1)–Cl(4) 2.8611(8), Tb(2)–Cl(1) 2.6857(8), Tb(2)–Cl(6) 2.6903(8), Tb(2)–Cl(2) 2.7248(8), Tb(2)–Cl(4) 2.8765(8), Tb(3)–Cl(7) 2.6768(7), Tb(3)–Cl(3) 2.7079(8), Tb(3)–Cl(2) 2.7161(8), Tb(3)–Cl(4) 2.8455(8), Tb(4)–Cl(5) 2.7334(7), Tb(4)–Cl(6) 2.7724(7), and Tb(4)–Cl(7) 2.7813(7) Å and bond angles Tb(4)O(4)Tb(2) 115.91(9)°, Tb(4)O(4)Tb(3) 115.83(9)°, Tb(4)O(4)Tb(1) 115.26(8)°, Tb(2)O(4)Tb(3) 102.86(8)°, Tb(2)O(4)Tb(1) 102.60(7)°, and Tb(3)O(4)Tb(1) 102.41(8)°.

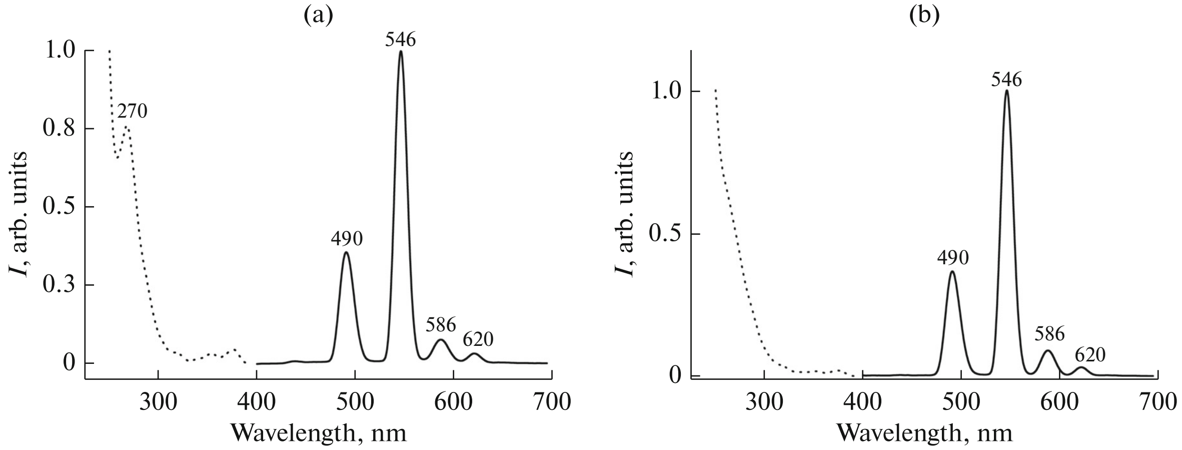


Fig. 2. (a) (······) Excitation (λ_{em} = 550 nm) and (——) fluorescence (λ_{exc} = 270 nm) spectra for complex **Ia**; (b) (······) excitation (λ_{em} = 550 nm) and (——) phosphorescence (λ_{exc} = 270 nm) spectra for complex **Ia**.

energy transfer from the organic ligand to the Tb^{3+} ions (antenna effect) is manifested in a range of 250–300 nm corresponding to the absorption range of the Cp ligand.

The phosphorescence kinetics of complex **Ia** is described by the monoexponential model. The characteristic lifetime of the excited state of the Tb^{3+} ion is fairly long and equal to 0.85 ms (±10%), which is typical of the Tb(III) complexes that demonstrate bright luminescence [18].

Thus, it is found that during careful hydrolysis the Cp compounds of terbium can form tetranuclear tetrahedral complexes. In this polynuclear complex, the cyclopentadienyl ligand can act as a ligand-“antenna” providing intensive luminescence.

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