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Inorganic chemistry**MIXED LIGAND COMPLEX COMPOUNDS OF TERBIUM WITH
HYDROXYNAPHTHOIC ACID****A.N.Gurbanov, S.S.Yusifova**

(Presented by Academician of ANAS R.A.Alieva)

We have synthesized complex compounds of terbium with 2-hydroxy-3-naphthoic acid of the composition $Tb(OHA)_3 \cdot nAm \cdot xH_2O$, where OHA – anion 2-hydroxy-3-naphthoic acid, Am – 1,10-phenanthroline ($n=2$; $x=1$); 2,2'-dipyridyl, diphenylguanidine ($n=1$; $x=2$), H_2O ($n=0$; $x=2$). Spectral-luminescent properties of obtained compounds were studied. It was determined that the compounds are thermally stable up to $280^\circ C$. By IR-spectroscopy method it was defined that hydroxynaphthoic acid is bidentate in hydroxynaphthoates of terbium.

Keywords: spectra, adsorption, luminescence, hydroxynaphthoic acid, terbium, X-ray pattern

The present work is the continuation of studying the properties of rare earth element complexes with aromatic carboxylic acids. Information on obtaining of complex compounds of rare earth elements with hydroxynaphthoic acid is limited [1]. It is known that isomeric hydroxynaphthoic acids, (OHA) in which substituents are in ortho position, form rather stable complexes with metal ions [2].

In the work we described the synthesis and studied spectral-luminescent properties of compounds of terbium with oxygen and nitrogen containing neutral ligands. Composition: $Tb(OHC)_3 \cdot nAm \cdot xH_2O$, where OHA - anion 2-hydroxy-3-naphthoic acid; Am-1,10-phenanthroline (millet), ($n=2$; $x=1$), 2,2' - dipyridyl (2,2'-Dipy), diphenylguanidine (DPG) ($n=1$; $x=2$), H_2O ($n=0$; $x=2$).

Experimental part

For the synthesis of compounds we used the following preparations "pure": $Tb(NO_3)_3 \cdot 6H_2O$, hydroxynaphthoic acid, nitrogen containing (phen, Dipy, DPG) compounds. Synthesis of mixed ligand complexes was conducted by the following technique: 3 mol OHC was added into 3 mol NaOH which was dissolved in minimum quantity of water. Then 1 mol $Tb(NO_3)_3 \cdot 6H_2O$ which was dissolved in 10-15 ml H_2O was added into the mixture, and 2 mol neutral ligand Am was poured into 10-20 ml 96% ethyl alcohol. pH of reaction mixture was brought to 5~6

0,1 m with solution of NaOH and kept until solid precipitated. The precipitate was filtered off, washed with water and dried in the opened air. Yield is 76-80%. Compounds are fine-crystalline red powders, compounds $Tb(OHA)_3 \cdot DPG \cdot 2H_2O$ are X-ray amorphous. X-ray studies of the compounds confirmed their individuality (table 1). Phase analysis has revealed the absence of lines of initial agents and mixtures.

Content (found/calculated), %:

1. $Tb(C_{33}H_{21}O_9) \cdot 2H_2O$; Tb - 20,60/20,75; C - 51,60/51,40; H - 3,66/3,26.
2. $Tb(C_{33}H_{21}O_9)(C_{24}H_{16}O_9) \cdot 2H_2O$; Tb - 14,40/14,50; C - 62,80/62,40; N - 5,0/5,10; H - 3,30/3,37.
3. $Tb(C_{33}H_{21}O_9)(C_{10}H_8N_2) \cdot 2H_2O$; Tb - 17,40/17,43; C - 56,6/56,57; N - 3,0/9,07; H - 3,44/3,62.
4. $Tb(C_{33}H_{21}O_9)(C_{13}H_{13}N_3) \cdot 2H_2O$; Tb - 16,42/16,44; C - 57,0/57,08; N - 4,30/4,34; H - 3,86/3,92.

IR-spectra were registered in device Specord - M80. Samples were prepared in the form of tablets with KBr. Electron compounds do not decompose. ESA of solutions were taken on Specord M80 in 200-400 nm range. Concentration of the compound in 96% of CuK_α - radiation.

Table 1

X-ray data for complexes of terbium with 2,3 – hydroxynaphthoic acid and amines

Tb(OHA) ₃ ·2H ₂ O		Tb(OHA) ₃ ·Phen·H ₂ O		Tb(OHA) ₃ -DPG-2H ₂ O		Tb(OHA) ₃ -Dipy·2H ₂ O	
d, Å	J/J ⁰	d, Å	J/J ⁰	d, Å	J/J ⁰	d, Å	J/J ⁰
14,46	59,60	11,76	72,8	12,59	100,0	11,06	100
12,97	92,3	10,65	73,3	10,40	20,8	10,11	37,8
10,04	16,4	9,93	100	9,58	13,2	9,76	43,3
6,54	22,0	9,30	56,5	8,65	20,8	9,30	51,1
6,06	100	8,81	33,3	8,26	17,0	8,04	72,2
5,60	15,2	6,92	30,0	6,30	17,0	7,66	74,4
5,35	20,3	5,75	20,0	5,71	24,5	7,02	10,0
5,06	16,4	5,29	23,3	5,53	18,9	5,64	43,4
4,68	36,9	4,70	33,3	5,28	15,1	5,52	52,2
4,34	10,9	4,43	36,7	4,92	32,1	5,35	8,9
4,10	43,8	4,10	30,0	4,50	15,1	5,18	32,2
4,05	17,8	3,88	23,3	3,94	13,2	4,92	13,3
3,76	10,4	3,42	26,7	3,72	15,2	4,58	25,6
3,32	82,2	–	–	3,24	13,2	4,20	4,89
2,40	13,7	–	–	–	–	2,10	12,2

Table 2

Important vibrational frequencies (CM⁻¹) in IR-spectra of hydroxynaphthoates

OHA	Tb(OHA) ₃ ·2H ₂ O	Tb(OHA) ₃ ·2Phen·H ₂ O	Tb(OHA) ₃ -Dipy·2H ₂ O	Tb(OHA) ₃ -DPG-2H ₂ O	Assignment
3047	3300	3407	3415	3465	ν(H ₂ O)
	3047	3059	3068	–	ν(CH)
	2968	2976	2952	–	ν(OH)
	1606	1613	1614	1614	δ(H ₂ O)
1686	–	–	–	1674	ν(C=O)
	1581	1589	1592	1645	ν _{as} (COO ⁻)
1575	1510	1518	1487	1534	ν(C=C)
–	–	–	–	3384	ν(NH)

Results and their discussion

Obtained compounds do not decompose – they are thermally more stable (up to 280°C). Important vibration frequencies in IR-spectra of hydroxynaphthoates are given in the table 1. Comparative analysis of IR-spectra of complexes and OHA allowed us to determine a coordination technique of hydroxynaphthoate-ion to central metal atom.

Intensive bands in the region 1580-1596 and 1455-1550 cm⁻¹ may be related to valence vibrations ν_{as}(COO⁻) and (C=O) of naphthalene ring.

Adsorption is observed in the region 1403-1414 cm⁻¹ [3, 4]. Frequency difference Δν=ν_{as}(COO⁻) - ν_s(COO⁻) is found to be – 180 cm⁻¹, which conforms to bidentate-bridge coordination of carboxylic groups with rare earth elements [5]. Adsorption with less intensity at 1571 and 1564 cm⁻¹ in IR-spectra of Tb(OHA)₃·2Phen·H₂O and Tb(OHA)₃·Dipy·2H₂O was caused by valency vibrations of bond C=C and C=N of neutral ligand (phen, Dipy). In the region 3100-3500 cm⁻¹ in spectra of complexes we observed blurred band caused by valence vibrations of water. Vibrations of Ln-O, Ln-N

in hydroxynaphthoates of terbium lie below 400 cm^{-1} . In IR-spectra of compounds $\text{Tb(OHA)}_3\cdot\text{DPG}\cdot 2\text{H}_2\text{O}$ the bands of $\nu(\text{C}=\text{O})$ with average intensity of nearly 1676 cm^{-1} appear in addition to the bands of $\nu_{\text{as}}(\text{COO}^-)$. In spectra of OHA – this vibration appears with 1686 cm^{-1} . These data are more likely to show the realization of bidentate coordination of hydroxynaphthoate-ion in these compounds. According to the data [6], bands with 3380 and 3480 cm^{-1} in IR-spectrum of free DPG are related to valence vibrations of NH-groups. During complex formation these frequencies decrease to 94 cm^{-1} , which indicates the coordination of DPG to terbium atom through NH group. Displacement of adsorption bands of these ligands towards large frequencies comparing with their position in spectra of free Phen and Dipy shows the coordination of molecules of Phen, Dipy terbium atom in complexes. In IR-spectrum of $\text{Tb(OHA)}_3\cdot 2\text{Phen}\cdot\text{H}_2\text{O}$ adsorption bands of Phen ($400, 620, 1560$ and 1590 cm^{-1}) shift towards large frequencies $7\text{--}11\text{ cm}^{-1}$, but out-of-plane due to overlapping them with adsorption bands of other ligands, in the region of $1580\text{--}1568\text{ cm}^{-1}$ the intensive bands $\nu_{\text{as}}(\text{COO}^-)$ appear, which conceal the bands $\delta(\text{CH})$ of the ring. Vibration $\delta(\text{CNH})$ Dipy lies on 1430 cm^{-1} . As it is seen from the figure 1 complex formation occurs when position of band shape is lower, which conforms to $\pi\text{--}\pi^*$ transition, and ESA of OHA ($\lambda_{\text{mak}}=340\text{--}360\text{ nm}$). For obtained hydroxynaphthoates of terbium more complex form of ESA is peculiar than for 2,3 oxynaphthoic acid. In ESA of $\text{Tb(OHA)}_3\cdot 2\text{Phen}\cdot\text{H}_2\text{O}$ and $\text{Tb(OHA)}_3\cdot\text{Dipy}\cdot 2\text{H}_2\text{O}$ we observed additional adsorption bands which are peculiar for coordinated neutral molecules. Adsorption bands of Dipy ($\lambda_{\text{mak}}=240\text{--}260\text{ nm}$) appear in the spectrum of $\text{Tb(OHA)}_3\cdot\text{Dipy}\cdot 2\text{H}_2\text{O}$. In the spectrum of $\text{Tb(OHA)}_3\cdot 2\text{H}_2\text{O}$ adsorption bands OHA^- due to singlet $\pi\text{--}\pi^*$ transition ($285\text{--}300\text{ nm}$) [6] is removed to more long-wave region comparing with its position in the spectrum of «free» hydroxynaphthoic acid. Hydroxynaphthoates of terbium luminesce (in solid state) both at room temperature and at 88 K . General character of luminescence spectra by a number of hydroxynaphthoates of terbium with neutral ligands is maintained.

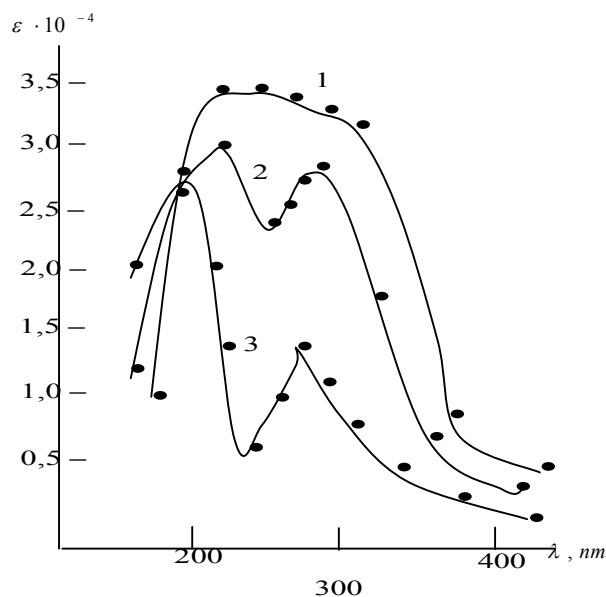
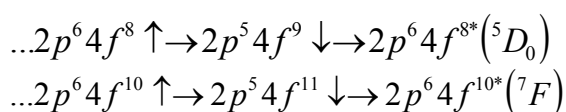


Fig. 1. Electron spectra of adsorption of 10^{-4} M solutions ($\text{C}_2\text{H}_5\text{OH}$).

1 – $\text{Tb(OHA)}_3\cdot\text{Dipy}\cdot 2\text{H}_2\text{O}$; 2 – $\text{Tb(OHA)}_3\cdot 2\text{H}_2\text{O}$;
3 – HOHA

In luminescence spectra of terbium complexes the more intensive bands are related to electro-dipole $^5D_0\text{--}^7F_6$ transition. This transition is more sensitive to substitution of neutral ligand. In mixed ligand complexes we observed redistribution of intensity of separate lines and changes in the structure, splitting of Stark components $^7F_6$. In luminescence spectra in the region of $^5D_0\text{--}^7F_6$ transition ($15920\text{--}16440\text{ cm}^{-1}$) 5-6 components are observed. Band intensity of magnetic-dipole transition $^5D_0\text{--}^7F_6$ is lower than band intensity of electro-dipole $^5D_0\text{--}^7F_6$ transition, and intensity of the latter in spectra of hydroxynaphthoates increases in a series of $\text{Tb(OHA)}_3\cdot\text{Dipy}\cdot 2\text{H}_2\text{O}$, $\text{Tb(OHA)}_3\cdot 2\text{H}_2\text{O}$, $\text{Tb(OHA)}_3\cdot 2\text{Phen}\cdot\text{H}_2\text{O}$, which shows that distortion degree of coordination polyhedron Tb^{3+} increases. Splitting of two extreme bands of magnetodipole $^5D_0\text{--}^7F_6$ transition essentially changes when neutral ligand varies. Value of ΔF luminescence spectra of complexes increases from $\text{Tb(OHA)}_3\cdot\text{Dipy}\cdot 2\text{H}_2\text{O}$, $\text{Tb(OHA)}_3\cdot\text{DPG}\cdot 2\text{H}_2\text{O}$, $\text{Tb(OHA)}_3\cdot 2\text{Phen}\cdot\text{H}_2\text{O}$, $\text{Tb(OHA)}_3\cdot 2\text{H}_2\text{O}$. In analogues row of hydroxynaphthoates

Tb(OHA)₃·Dipy·2H₂O, Tb(OHA)₃·2Phen·H₂O and Tb(OHA)₃·2H₂O the variation of neutral ligand does not lead to essential change of relations of integral bands $^5D_0-^7F_6$ and $^5D_0-^7F_6$ transitions to intensity of a band of $^5D_0-^7F_6$ transition. If we consider the formation of luminescent properties of mixed ligand compounds of terbium within a model of direct change by unpaired electrons then the excitation mechanism of luminescence (Tb III) schematically is as follows:



For band assignment in excitation spectra of complexes the data on the adsorption spectra of separate fragments are necessary. In ESA of hydroxynaphthoates of terbium (fig. 1) only bands of $S\pi-\pi^*$ (340-360 nm) transitions appear more intensively. Longer bands caused by $n-\pi^*$ transitions could not be observed due to less intensity in adsorption spectra and possible displacement of short-wave region [6]. It is known that during substitution of H atom to OH group in naphthalene molecule, the nature of long-wave electron bands of spectrum changes: $n-\pi^*$ bands disappear, and long-wave band becomes $\pi-\pi^*$ band in the region of 320-380 nm.

Probability of excitation of hydroxynaphthoates of rare earth element bands in the spectra caused by $\pi-\pi^*$ transition of lone-pair

$2P_z$ - electrons of heteroatom $\pi-\pi^*$ ($2P_z$) band should not be excluded. By its photo chemical behavior this state is nearer to $\pi-\pi^*$ state than to $n-\pi^*$, so corresponding band $\pi-\pi^*$ ($2P_z$) should have a rather high intensity.

All the above statements do not allow us to give one-to-one relation of a wide band with maximum 430 nm k $n-\pi^*$ or $\pi-\pi^*$ ($2P_z$) transition which demands an additional investigation of photo chemical activity of hydrogen atom abstraction.

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Azerbaijan State Pedagogical University

TERBİUMUN HİDROKSİNAFTOY TURŞUSU İLƏ MÜXTƏLİFLİQANDLI KOMPLEKS BİRLƏŞMƏLƏRİ

Ə.N.Qurbanov, S.S.Yusifova

Terbiumun 2-hidroksi-3 naftoy turşusu ilə Tb(ONK)₃·nAm·Xn₂O tərkibli kompleks birləşməsi sintez olunmuşdur. Kompleksdə ONK 2-hidroksi-3-naftoy turşusunun anionu, Am-1,10-fenantrolin (n=2; x=1); 2,2'-dipiridil, difenilquandil (n=1; x=2), H₂O (n=0; x=2).

Alınan birləşmənin spectral-lüminesensiya xassələri öyrənilmişdir.

Müəyyən edilmişdir ki, birləşmə 280°C-yə qədər davamlıdır. İQ-spektroskopik metodla müəyyən edilmişdir ki, terbium hidroksinaftoy kompleksində hidroksinaftoy turşusu bidentatdır.

Açar sözlər: spektr, udma, terbium, hidroksinaftoy turşusu, rentgenoqram

**РАЗНОЛИГАНДНЫЕ КОМПЛЕКСНЫЕ СОЕДИНЕНИЯ ТЕРБИЯ
С ГИДРОКСИНАФТОЙНОЙ КИСЛОТОЙ****А.Н.Гурбанов, С.С.Юсифова**

Синтезированы комплексные соединения тербия с 2-гидрокси-3-нафтойной кислотой состава $Tb(OHA)_3 \cdot nAm \cdot xH_2O$, где ОНК – анион 2-гидрокси-3-нафтойной кислоты, Ам – 1,10-фенантролин ($n=2$, $x=1$), 2,2-дипиридил, дифенилгианидин ($n=1$, $x=2$), H_2O ($n=0$; $x=2$). Изучены спектрально-люминесцентные свойства полученных соединений. Установлено, что соединения термически устойчивы до $280^\circ C$. Методом ИК-спектроскопии установлено, что гидроксинафтойная кислота в гидронафтоатах тербия бидентатна.

Ключевые слова: спектр, поглощение, люминесценция, гидроксинафтойная кислота, тербий, рентгенограмма