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Preparation and Properties of the $M^{III}U_2O_{7.5}$ Polyuranates (M^{III} = Y, Tb, Dy, Ho, Er, Tm, Yb, or Lu)

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Abstract—The novel compounds of the $M^{III}U_2O_{7.5}$ type (with M^{III} being yttrium or lanthanides from terbium to lutetium) have been prepared via hydrothermal synthesis from hydrated uranium(VI) oxide and aqueous solutions of M(III) nitrates at 200°C. Composition and structure of the products have been studied by means of elemental analysis, high-temperature X-ray diffraction, and IR spectroscopy; the products thermal stability has been estimated.

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Recently, the preparation of $M^{III}U_3O_{10.5}\cdot 6H_2O$ polyuranates (with M^{III} being the elements from La to Sm) was reported [1]. The products were all of layered structure, and revealed similar composition and crystallographic parameters. However, the attempts to prepare the corresponding polyuranates of europium, gadolinium, and further rare earth elements failed [1].

Extending that study, here we report on preparation, composition, structure, and some properties of polyuranates of a series of elements from terbium to lutetium, and of yttrium. All the compounds were isolated as individual crystalline phases, and their elemental composition was determined as well as the crystallographic parameters. The range of crystal-chemical parameters of M^{III} capable of formation of that polyuranates type was estimated.

To the very best of our knowledge, the information on formation of polyuranates with yttrium group lanthanides (Tb to Lu) has not been reported in the literature so far.

Due to the lanthanide contraction, the ionic radii (according to Belov and Bokii) of the M^{III} decreased with the atomic number from 1.02 Å (Ce) down to 0.80 Å (Lu). The radii difference reached 22%, and therefore composition and structure of the formed compounds were different. In the group of cerium rare earth elements, the ratio of ionic radii of cerium (1.02 Å) and gadolinium (0.94 Å) to that of oxygen (1.36 Å) ranged from 0.71 to 0.75. Such ratio was typical of the coordination number of 7 or higher. In the group of yttrium rare earth elements, the respective ratios in the cases of terbium (0.65) and lutetium (0.59) were characteristic of compounds with the cation coordination number of 6. Therefore, formation of the compounds with identical composition and structure within the whole series of rare earth elements (including lanthanum and yttrium) was hardly probable.

As was shown in [1], the interaction of hydrated uranium(VI) oxide with aqueous solutions of La(III), Ce(III), Pr(III), Nd(III), and Sm(III) salts under hydrothermal conditions led to polyuranates of similar composition and structure, whereas in the cases of Eu(III) and Gd(III) salts the same reaction gave poorly matured phases with many non-identified admixtures. Further elements (terbium to lutetium) formed well-defined individual crystalline phases again.

The elemental compositions of the formed phases are collected in Table 1 along with the respective ratios of ionic radii $r(M^{3+})/r(O^{2-})$; that ratios were used to predict the most probable coordination number of the M^{III} cations. As followed from the tabulated data, all the prepared compounds revealed similar composition, $M^{III}U_2O_{7.5}$.

The $r(M^{3+})/r(O^{2-})$ ratios ranged in between 0.41 and 0.73, being typical of coordination number of 6. Therefore, all the compounds were likely structurally similar as well.

Table 1. Elemental composition of the $M^{III}U_2O_{7.5}$ polyuranates

M^{III}	$M^{III}_2O_3$, wt %		UO_3, wt %		$r(M^{3+})$[a], Å	$r(M^{3+})/r(O^{2-})$[b]
	found	calculated	found	calculated		
Y	16.31	16.48	83.47	83.52	0.97	0.71
Tb	24.17	24.23	75.58	75.77	0.89	0.65
Dy	24.48	24.59	75.33	75.41	0.88	0.64
Ho	24.74	24.83	75.07	75.17	0.86	0.63
Er	24.99	25.06	74.83	74.94	0.85	0.62
Tu	25.11	25.22	74.67	74.78	0.85	0.62
Yb	25.55	25.62	74.28	74.38	0.81	0.59
Lu	25.71	25.80	74.14	74.20	0.80	0.59

[a] Ionic radii are given according to Belov and Bokii. [b] $r(O^{2-})$ = 1.36 Å.

Table 2. X-ray diffraction parameters of the $M^{III}U_2O_{7.5}$ polyuranates

Y		Tb		Dy		Ho		Er		Tu		Yb		Lu	
d, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %
4.129	37	4.179	4.175	4.169	36	4.156	33	4.152	33	4.133	31	4.128	39	4.099	36
3.529	9	3.551	8	3.5147	6	3.537	8	3.531	6	3.529	7	3.485	8	3.489	8
3.425	100	3.439	100	3.437	100	3.437	100	3.436	100	3.432	100	3.430	100	3.429	100
3.188	8	3.189	12	3.180	19	3.184	23	3.181	21	3.188	18	3.185	19	3.183	12
2.833	6	2.861	8	2.856	6	3.845	9	2.857	8	2.855	6	2.855	8	2.860	7
2.637	56	2.650	59	2.649	59	2.650	50	2.637	51	2.635	53	2.630	58	2.629	56
2.059	7	2.087	8	2.085	6	2.077	7	2.067	8	2.063	5	2.059	8	2.057	6
1.976	15	1.989	12	1.987	12	1.984	14	1.991	14	1.981	13	1.977	12	1.971	16
1.921	10	1.963	8	1.963	9	1.934	6	1.936	6	1.931	7	1.929	7	1.929	8

The phase purity and structural similarity of the studied compounds was confirmed by the X-ray diffraction data shown in Table 2.

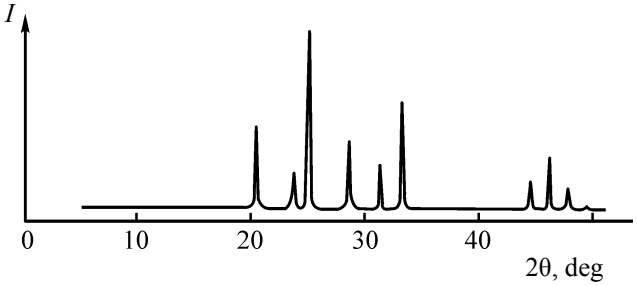
All the performed syntheses were reproducible, and all the corresponding X-ray diffraction patterns revealed close interlayer spacing and the diffraction maxima intensity.

As a representative example, the holmium diuranate diffraction pattern is shown in the figure. No diffraction maxima were found at small 2θ angles (that would be typical of uranyl compounds); therefore, we concluded that the layered structure was not typical of polyuranates of the yttrium group metals.

The IR spectra of all the studied compounds contained the only absorption band at 868–871 cm^{-1} assigned to the ν_{as} of $[O\cdots U\cdots O]^{2+}$:

M^{III}	Y	Tb	Dy	Ho	Er	Tu	Yb	Lu
$\nu_{as}(UO_2)^{2+}$, cm^{-1}	881	871	871	869	871	868	870	871

According to the reference data, the $\nu_{as}(UO_2)^{2+}$ band was located at 935–940 cm^{-1} in the case of uranium-oxygen polyhedron [U(VI) coordination number being of 6]. With the coordination number



X-ray diffraction pattern of holmium polyuranate $HoU_2O_{7.5}$.

increased to 7, the U⋯O bonds in uranyl were elongated, and the absorption band wavenumber decreased to 900–915 cm^{-1} [2]. The $\nu_{as}(UO_2)^{2+}$ absorption bands shift to even lower wavenumbers (868–871 cm^{-1}) observed in this work was due to the U⋯O bonds elongation as well. Hence, the uranyl group could not efficiently facilitate the layered structure formation. The frame structure of the $M^{III}U_2O_{7.5}$ compounds was confirmed by the X-ray diffraction experiments at 20–1000°C. All the studied compounds revealed high thermal stability: the well-defined diffraction patterns were preserved at up to 900°C. At higher temperatures, the $M^{III}U_2O_{7.5}$ were transformed into complex oxides $M^{III}_2O_3 \cdot 4UO_3$.

To conclude, in this work we demonstrated the formation of structurally similar $M^{III}U_2O_{7.5}$ compounds (with M^{III} being Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu). The structural and compositional similarity of the prepared compounds was mainly due to the close ionic radii of the studied metals.

EXPERIMENTAL

The hydrated uranium(VI) oxide was introduced into the reaction in the form of synthetic schoepite prepared as described elsewhere [3]. A weighed schoepite specimen (0.5 g) was added to 100 mL of the M^{III} nitrate solution (0.5 mol/L). The synthesis was performed in a Teflon ampoule, in the steel autoclave, at 200°C during 10 h. The formed precipitate was filtered off, washed with distilled water, and dried in air at 25°C.

The compounds composition was determined as follows. The weighed polyuranate specimen was dissolved in sulfuric acid, and uranium concentration in the prepared solution was measured by means of spectrophotometry after reaction with arsenazo III (λ_{max} = 650 nm, pH = 3) [4]. The M^{III} concentration was determined by titration with Trilon B solution (10^{-3} mol/L) in the presence of Xylene orange; the equivalence point was found as intersection of the linear sections of the photometric titration curve [5].

The optical spectroscopy measurements were performed with UV-1650 spectrophotometer (Shimadzu). The X-ray diffraction patterns were registered with XRD-6000 diffractometer equipped with high-temperature attachment HA-1001 (Shimadzu). IR spectra were recorded with FTIR-8400S spectrometer (Shimadzu).

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