

# Synthesis of Bismuth (III) Oxide Salicylate from Nitrate Solutions for Medical Purposes

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(Received December 22, 2008; revised February 17, 2009)

## Abstract

By means of X-ray phase analysis, IR and Raman spectroscopy, thermogravimetry and chemical analysis, precipitation of bismuth salicylate from its nitrate solutions and the interaction of trihydroxo-pentaoxo-hexabismuth (III) pentanitrate trihydrate  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with the solutions of sodium salicylate and salicylic acid were studied. The rate of nitrate ion exchange for salicylate ion depending on temperature and pH of the medium was investigated. The conditions for the formation of bismuth (III) oxide salicylate with the composition  $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)\text{O}$  during precipitation from nitrate solutions and according to the reaction solid-solution were determined. For use as medical substances of antiulcerants and antidiarrheal agents, the reasonableness of the synthesis of this compound in the high-purity state by means of the interaction of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with the solution of salicylic acid was demonstrated.

**Key words:** bismuth (III) oxide salicylate, synthesis, IR and Raman spectra, thermal analysis

## INTRODUCTION

Bismuth compounds are used in medicine since the end of the 18th century as medical substances to treat various gastrointestinal diseases. In 1990, a liquid preparation containing bismuth subsalicylate as the medical substance was developed for the first time in the USA [1]. At present, bismuth (II) oxide salicylate (bismuth subsalicylate)  $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)\text{O}$  [2] is a component of colloid suspensions of medical antiulcer and antidiarrheal preparations Desmol, Pepto-Bismol and Bismatrol. Bismuth (III) oxide salicylate is transformed in the gastrointestinal tract into salicylic acid and different bismuth salts that form insoluble protective coatings at the sites of ulcer localization [1].

Various methods of obtaining bismuth (III) oxide salicylate were described [3–5]. A compound with the composition  $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)_3 \cdot 4\text{H}_2\text{O}$  [3] was synthesized through the interaction of neutral bismuth (III) nitrate with sodium salicylate in glycerol; as a result of washing with

ethanol or acetone, a compound with the composition  $\text{Bi}_4(\text{C}_7\text{H}_5\text{O}_3)_6\text{O}_3 \cdot \text{H}_2\text{O}$  is formed. It was also proposed to obtain bismuth (III) oxide salicylate by boiling a mixture of 9.4 g of bismuth oxide and 9.4 g of salicylic acid in the presence of water for 6 h [3]. The author of [4] thinks that the interaction of bismuth hydroxide, obtained from neutral bismuth nitrate by precipitation with ammonia, with salicylic acid at 90 °C results in the formation of the compound with the composition  $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)\text{O}$ . A multistage process of the synthesis of compound with the composition  $[\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)\text{O} + \text{Bi}_2\text{O}_3]$  from  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was described in monograph [5]. Bismuth (III) trinitrate pentahydrate is dissolved in nitric acid. The resulting solution is mixed with the aqueous solution of ammonia, the formed precipitate is washed with ammonia solution to remove nitrate ions, then the precipitate is multiply washed with water and treated with salicylic acid under heating. Investigation of the process of bismuth deposition from chloric acid solutions, carried

out by us, showed [6] that bismuth can precipitate in the case of the addition of salicylate ions in the form of compounds having the composition  $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)\text{O}$  or  $\text{Bi}_2(\text{C}_7\text{H}_5\text{O}_3)_4\text{O}$ .

For the synthesis of bismuth compounds, it is usual to take bismuth-containing nitrate solutions obtained by dissolving the granules of the metal of Vi 1 grade in nitric acid with the concentration 7–9 mol/L. During bismuth precipitation from nitrate solutions, the problem of bismuth purification from accompanying metals that are able to co-precipitate arises [7, 8]. In this connection, it is of practical interest to study the process of bismuth (III) oxide salicylate precipitation directly from nitric solutions used to manufacture bismuth compounds, and also according to the reaction solid – solution using the compound with the composition  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  purified preliminarily from accompanying metals as the solid compound [8].

In the present work, we studied precipitation of bismuth (III) oxide salicylate from its nitric solutions depending on the molar ratio of salicylate ions and bismuth in solution, and the interaction of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with the aqueous solutions of sodium salicylate and salicylic acid depending on the process time and temperature.

## EXPERIMENTAL

The initial solutions of bismuth nitrate (330 g/L Bi, 110 g/L  $\text{HNO}_3$ ) were prepared by dissolving bismuth oxide of Os. Ch. 13-3 reagent grade in nitric acid of Os. Ch. 18-4 reagent grade. Mineral acids, salts and alkalis of Kh. Ch. or Os. Ch. reagent grade were used in the work. Hydrolytic precipitation of bismuth from nitrate solutions and investigation of the interaction of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with the solutions of sodium salicylate and salicylic acid was carried out in Teflon vessels equipped with mixers. Thermostating was carried out with water baths WB-2. Precipitation of bismuth (III) oxide salicylate from nitric solutions was performed by adding the corresponding bismuth-containing solution to the aqueous solution of sodium salicylate. The ratio of the volumes of initial and final solution was 1 : 10 (it was corrected by adding distilled water). The mixture was stirred for 1 h. The precipitate was sepa-

rated by filtering, washed with distilled water and dried in the air.

Trihydroxo-pentaoxo-hexabismuth (III) pentanitrato trihydrate with the composition  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  (bismuth content 72.28 %, nitrate ions 17.38 %) was obtained by diluting the initial bismuth-containing solution with water at a ratio of 1 : 40, the mixture was stirred for 1 h. The precipitate was washed with distilled water and thoroughly filtered under vacuum. Bismuth content in the product was determined after its dissolution in nitric acid (1 : 1).

Investigation of the interaction of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  was carried out in the solution containing 20–25 g of bismuth per 500 mL of solution. Weighed portions of sodium salicylate or salicylic acid at a temperature of  $(23 \pm 2)^\circ\text{C}$  and  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  were added to water, then the process was studied at a given temperature. The initial molar ratio of salicylate ions to bismuth was 1 : 1. The resulting exchange products were washed two times with distilled water during mixing; the precipitate was separated by filtering and dried in the air.

X-ray phase analysis (XPA) of the products was carried out with DRON-3 diffractometer using  $\text{CuK}_\alpha$  radiation, the frequency of counter rotation was 0.5 deg/min. The curves of differential thermal analysis (DTA) and mass changes (TG) of the samples under investigation were recorded with MOM derivatograph (Hungary) at the heating rate of  $10^\circ\text{C}/\text{min}$ . The IR absorption spectra were recorded within the range  $400\text{--}4000\text{ cm}^{-1}$  with a Specord IR-75 spectrophotometer. The samples were prepared as tablets with annealed KBr. The Raman spectra were recorded using a Bruker RFS 100/S spectrometer equipped with Nd:YAG laser (maximal power 5 W,  $1.064\text{ }\mu\text{m}$ ). Electron microphotographs of the products were taken by transmission electron microscopy (Jeol JEM 2000FXII) with accelerating voltage of 200 kV. The solution pH was measured on an OP-264/1 digital pH-meter (Hungary) with the help of the glass electrode.

Determination of the macro-amounts of bismuth in solutions was carried out by titration with complexon III solution using xylenol orange as an indicator, micro-amounts were determined by means of photocolormetry with potassium iodide [9]. The products of reactions

were preliminarily dissolved in diluted  $\text{HNO}_3$  (1 : 1). Determination of the anions of salicylic acid and nitrate ions in the solid products of reactions was carried out after their transfer into solution of 2 M NaOH at 70–90 °C. The content of salicylate ions and free salicylic acid in precipitates was determined by means of photocolorimetry [10]. Determination of free salicylic acid was carried out after transfer into solution by treating the precipitate with ethanol. The concentration of nitrate ions was determined by means of photometry with sodium salicylate [11].

## RESULTS AND DISCUSSION

Investigation of the precipitation of bismuth (III) oxide salicylate from nitric solutions with salicylic acid was carried out at 70 °C, due to its low solubility in water under usual conditions, and at the molar ratio of salicylate ions to bismuth equal to 1 : 1. Under these conditions, the degree of bismuth precipitation is 61.2 % (for equilibrium pH 0.4). According to X-ray data, the precipitates are bismuth (III) oxide salicylate, but the colouring of the precipitates is rose, may be due to partial nitration of salicylic acid and the formation of its nitro derivatives [13]. The content of nitrate ions in precipitates is 0.074 %.

Further studies of the precipitation of bismuth (III) oxide salicylate were carried out after neutralization of salicylic acid into sodium salicylate with NaOH solution. Investigation of the precipitation of bismuth (III) oxide salicylate from nitrate solutions by adding the bismuth-containing solution to sodium salicylate at a temperature of 23 and 70 °C and mixing time 1 h showed that the degree of bismuth precipitation depends on the introduced amount of salicylate ions. With an increase in the concentration of salicylate ions, the degree of bismuth precipitation ( $R$ ) increases. For the molar ratio of salicylate ions to bismuth in solution ( $n$ ) equal to 1 : 1, and process temperature 23 °C, the degree of bismuth precipitation is 77.0 %, pH 0.8. According to X-ray studies, the precipitate synthesized at 23 °C is a mixture of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  and the free salicylic acid. Precipitates obtained at 40 and 50 °C at

the given molar ratio of salicylate ions and bismuth are bismuth (III) oxide salicylate with an admixture of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ , the content of nitrate ions in the precipitates is 4.0 and 1.8 %, respectively. At 70 °C, we obtained the precipitate of bismuth (III) salicylate having the following composition, %: bismuth 57.6, salicylate ions 37.6, nitrate ions 0.032. Further temperature rise to 80 °C and above causes decomposition of the formed precipitates.

In the solution with  $n = 1.1$  at the process temperature of 70 °C, the degree of bismuth precipitation is 80.2 %, pH 0.9 (Fig. 1). With an increase in  $n$  in solution to 3.0, the degree of bismuth precipitation reaches 99.1 %, pH 1.0. Further increase in the concentration of salicylate ions in the system does not lead to any substantial increase in the degree of bismuth transition into the precipitate.

The results of X-ray studies of the products of bismuth precipitation provide evidence that the precipitate obtained at  $n < 1$  is a mixture of bismuth (III) oxide salicylate and  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with characteristic diffraction maxima with  $d/n$ , Å: 2.12, 3.29, 3.55, 6.73, 7.50, 13.60 (Fig. 2, curve 1). At the molar ratio of salicylate ions to bismuth in solution equal to 1 : 1, the precipitate is bismuth (III) oxide salicylate with the composition  $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)\text{O}$ , for which, according to XPA data [6], the following maxima are characteristic, with  $d/n$ , Å: 2.38, 2.78, 2.83, 3.33, 3.46, 3.68, 3.77, 4.16, 4.60, 5.43, 7.42, 8.30, 10.2, 11.0, 16.4 (see Fig. 2, curve 2). For  $n = 1.5$ , the product is a mixture of  $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)\text{O}$  with  $\text{Bi}_2(\text{C}_7\text{H}_5\text{O}_3)_4\text{O}$  having diffraction maxima with  $d/n$ , Å: 1.88, 2.06, 2.26, 2.31, 2.73, 3.15, 3.26, 3.99, 4.31, 4.44,

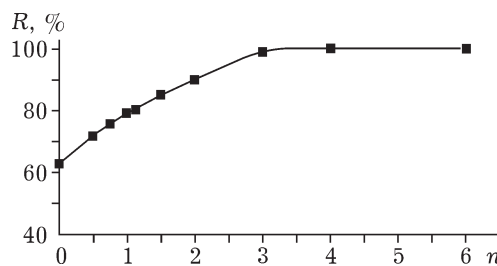


Fig. 1. Dependence of the degree of bismuth precipitation ( $R$ ) on the molar ratio of salicylate ions to bismuth ( $n$ ) in solution at 70 °C.

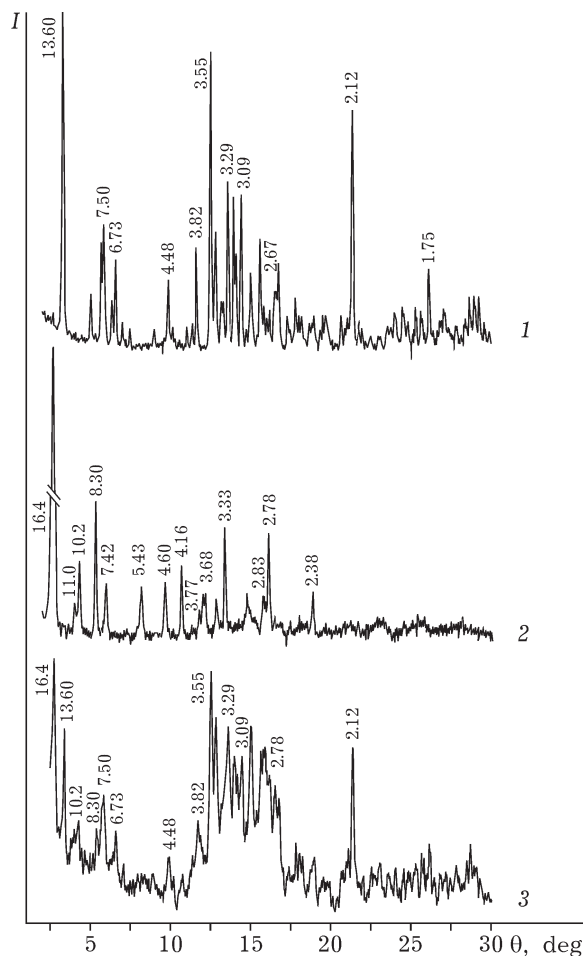


Fig. 2. Diffraction patterns of the products of bismuth precipitation: 1 –  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ , 2 – bismuth (III) oxide salicylate, 3 – precipitate obtained in the interaction of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with the solution of sodium salicylate at 70 °C for 1 h.

4.54, 4.99, 6.14, 6.77, 7.48, 14.9 [6]. With an increase in the molar ratio of salicylate ions to bismuth in solution to 2 and more, a compound with the composition  $\text{Bi}_2(\text{C}_7\text{H}_5\text{O}_3)\text{O}$  is formed as the reaction product.

In order to increase the degree of bismuth transfer into the precipitate, we studied the effect of solution pH on the degree of bismuth precipitation. On addition of bismuth solution into the water-alkaline solution of sodium salicylate at the molar ratio of salicylate ions to bismuth  $n = 1.1$  (pH 1.8), the degree of bismuth precipitation increases from 80.2 to 98.5 %, and the precipitate is bismuth (III) oxide salicylate with the composition, %: bismuth 57.3, salicylate ions 37.5, nitrate ions 0.013, the ratio of salicylate ions to bismuth in the precipitate is 1.0. At pH 2.2 the degree of bis-

moth precipitation is 99.7 %, with a decrease in the acidity of solution to pH 4.0 the degree of bismuth precipitation increases to 99.99 %. Further addition of alkali into the system does not cause changes in bismuth precipitation degree, but X-ray amorphous products with increased bismuth content are formed.

In the synthesis of high-purity bismuth compounds for medical properties, it is necessary to carry out preliminary purification of bismuth from accompanying metals by its precipitation from nitrate solutions in the form of compound with the composition  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  [8]. Due to the high coefficient of bismuth purification from accompanying metals in the hydrolysis of nitrate solutions, one may widely use  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  for the synthesis of high-purity bismuth compounds according to the reaction solid-solution.

Results of the investigation of the interaction of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with salicylic acid (Fig. 3, curves 1 and 4) and sodium salicylate (curves 2 and 3) at 70 °C showed that in the former case even after 15 min bismuth (III) oxide salicylate is formed, pH 1.2, bismuth concentration in solution 1.02 g/L, the composition of the precipitate, %: bismuth 57, salicylate ions 37.3, nitrate ions 0.047. After interaction for 1 h, the precipitates with nitrate ion content not more than 0.02 % were obtained. The molar ratio of salicylate ions to bismuth in the precipitates is 1.0, the precipitates are composed of bismuth (III) oxide salicylate, which is also confirmed by the data of X-ray phase analysis. The precipitates synthesized through the interaction of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with

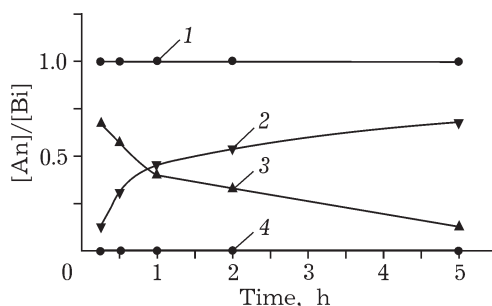


Fig. 3. Dependence of the ratio of salicylate (1, 2) and nitrate ions (3, 4) to bismuth in the precipitates on the time of the interaction of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with the solutions of salicylic acid (1, 4) and sodium salicylate (2, 3) at 70 °C.



salicylic acid for 1 h at a temperature of 23, 40 and 60 °C are mixtures of the compounds with the composition  $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)\text{O}$ ,  $\text{Bi}_2(\text{C}_7\text{H}_5\text{O}_3)_4\text{O}$  and  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ . With an increase in interaction time to 4 h at 23 and 40 °C one fails to obtain pure bismuth (III) oxide salicylate. The synthesized precipitates contain 8.93 and 5.05 % of nitrate ions, respectively; their diffraction patterns contain the diffraction maxima of  $\text{Bi}_2(\text{C}_7\text{H}_5\text{O}_3)_4\text{O}$  and  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ . According to X-ray data, the precipitate obtained at 60 °C is bismuth (III) oxide salicylate, admixture of nitrate ions in it is 0.12 %.

At a temperature of 23 °C,  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  exhibits almost no interaction with sodium salicylate. Thus, the precipitate obtained during the interaction for 1 h, according to XPA data, is the initial compound with nitrate ion content 16.8 %. With an increase in the temperature of reacting mixture to 70 °C, the reaction rate increases regularly. However, the precipitate synthesized during the interaction for 1 h is a mixture of bismuth (III) oxide salicylate and  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  containing bismuth 64.6 %, salicylate ions 19.0 % and nitrite ions 7.69 %, pH 5.65; bismuth content in solution is 0.0059 g/L. The diffraction patterns of the resulting product contains, in addition to the diffraction maxima of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ , additional diffraction maxima 16.4, 10.2, 8.30 Å, belonging to bismuth (III) oxide salicylate (see Fig. 2, curve 3). With an increase in the interaction time to 5 h, we failed to obtain a pure product, too (see Fig. 3, curves 2, 3).

Analysis of absorption IR and Raman spectra of the sample obtained in the interaction of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with sodium salicylate solution for 1 h at 70 °C (Fig. 4, *a*, *b*, curves 2) provides evidence of the start of the transition of the initial compound into bismuth (III) oxide salicylate. In the case of treatment of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with the solution of salicylic acid under similar conditions, the exchange proceeds completely (see Fig. 4, curves 3). The spectrum of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  (see Fig. 4, curves 1) within the range 1400–700  $\text{cm}^{-1}$  contains the bands characteristic of nitrate ion with the symmetry not higher than  $\text{C}_{2v}$  [14]:  $\nu_1$  at 1040 and 1030  $\text{cm}^{-1}$  (IR), 1057 and 1047  $\text{cm}^{-1}$  (Raman), prohibited in the IR spectrum of the

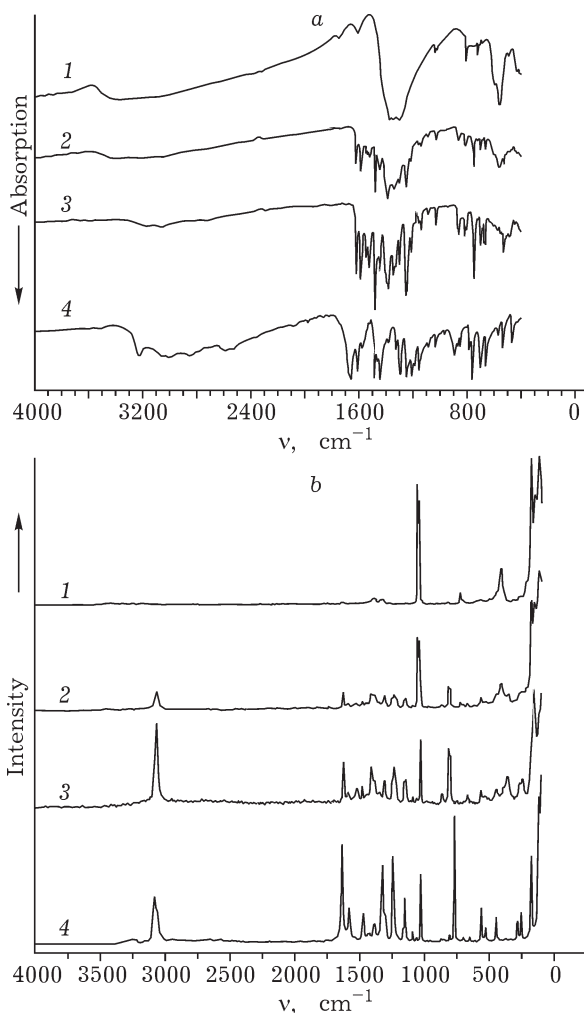


Fig. 4. IR (*a*) and Raman absorption (*b*) spectra of the products of bismuth precipitation: 1 –  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ ; 2 – precipitate obtained in the interaction of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with the solution of sodium salicylate at 70 °C for 1 h; 3 – bismuth (III) oxide salicylate; 4 – salicylic acid.

free nitrate ion ( $D_{3h}$ ),  $\nu_2$  at 810  $\text{cm}^{-1}$ ,  $\nu_3$  at 725 (IR) and 727  $\text{cm}^{-1}$  (Raman). An intense band with several maxima within the range 1420–1290  $\text{cm}^{-1}$  (IR) corresponds to the stretching antisymmetrical vibration  $\nu_3$  of the free nitrate ion. Broad diffuse absorption bands in the region 3600–3300  $\text{cm}^{-1}$  in the IR and Raman spectra of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  are to be related to the stretching vibrations of crystallization water and  $\text{OH}^-$  groups participating in strong hydrogen bonds. The band at 1620  $\text{cm}^{-1}$  (IR) corresponds to the bending molecules of crystal water molecules. An intense band with the maxima at 600 and 564  $\text{cm}^{-1}$  (IR) can be attributed to the fan vibrations of water mole-

cules [15]. The spectra of the sample obtained as a result of exchange for 1 h between  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  and the solution of sodium salicylate at 70 °C (see Fig. 4, curves 2) conserve the bands of the initial compound: intense bands in the region 1420–1290  $\text{cm}^{-1}$  (IR), and bands at 1057 and 1047  $\text{cm}^{-1}$  (Raman); absorption bands related to salicylate ion appear. In the spectra of the sample obtained as a result of exchange between  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  and the solution of salicylic acid for 1 h at 70 °C, we did not detect any bands characteristic of this compound. A comparison of the IR and Raman spectra of salicylic acid and bismuth (III) oxide salicylate (see Fig. 4, curves 3 and 4) shows that the protons in carboxylic groups of salicylic acid get substituted with Bi-containing cation. In the spectra of bismuth (III) oxide salicylate, the bands of asymmetrical  $\nu_{\text{as}}(\text{COO}^-)$  and symmetrical  $\nu_{\text{s}}(\text{COO}^-)$  stretching vibrations appear: in IR spectra at 1525, 1545 and 1390  $\text{cm}^{-1}$ , in Raman spectra at 1519, 1540 and 1414  $\text{cm}^{-1}$ , respectively. The bands of the stretching vibrations of carbonyl group  $\nu(\text{C}=\text{O})$  at 1660 (IR) and 1636  $\text{cm}^{-1}$

(Raman) that are present in the spectra of initial salicylic acid [16] now disappear, which is the evidence of the substitution of protons in the carboxylic group of the acid for Bi-containing cation. The difference  $\Delta\nu(\text{COO}^-) = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$  from the IR spectrum of bismuth (III) oxide salicylate is 135 and 169  $\text{cm}^{-1}$ , which points to predominantly bidentate [17] coordination of the salicylate ligand to metal cation.

In the IR spectrum of bismuth (III) oxide salicylate, the absence of a weak broad band in the region 2500–3000  $\text{cm}^{-1}$  related to the stretching vibrations  $\nu(\text{OH})_{\text{COOH}}$ , the bands of out-of-plane bending vibrations  $\delta_{\text{y}}(\text{OH})_{\text{COOH}}$  at 892  $\text{cm}^{-1}$ , scissor vibrations  $\delta(\text{OH})_{\text{COOH}}$  at 1445  $\text{cm}^{-1}$ , and the appearance of scissor vibrations of medium intensity  $\delta_{\text{s}}(\text{COO}^-)$  at 860  $\text{cm}^{-1}$  (IR), as well as the bands at 485 (IR), 365 and 391  $\text{cm}^{-1}$  (Raman) of stretching  $\nu(\text{Bi}-\text{O})$  vibrations [18], strong bands at 163  $\text{cm}^{-1}$  (Raman), bending vibrations  $\delta(\text{Bi}-\text{O})$  [19] provide evidence of the substitution of protons in the carboxylic group of salicylic acid by a Bi-containing cation.

The appearance of the bands of stretching vibrations  $\nu(\text{C}-\text{O})$  of phenol group at 1250  $\text{cm}^{-1}$

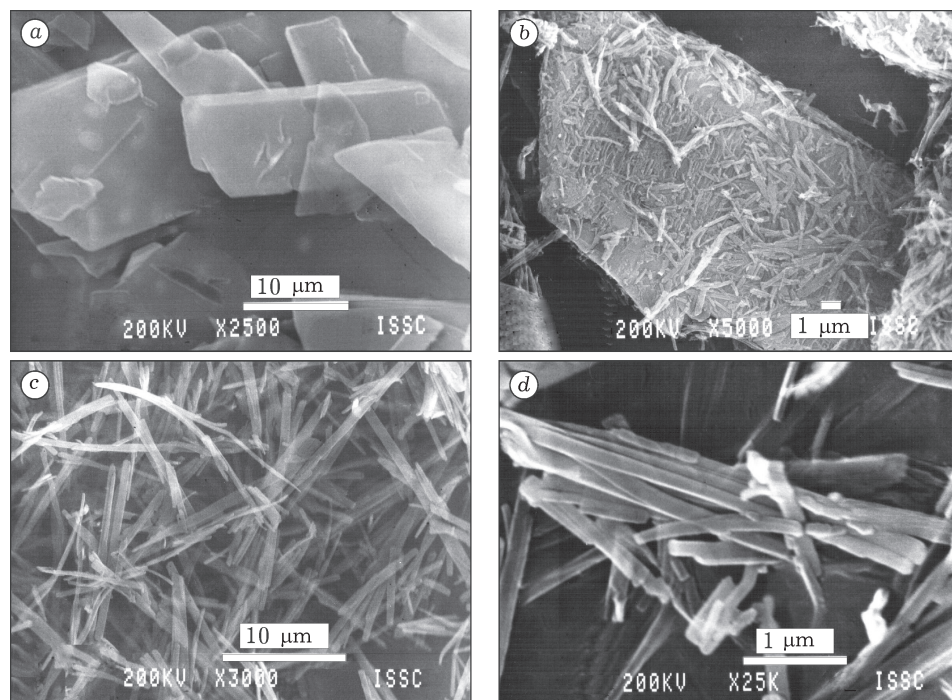


Fig. 5. Photomicrographs of the products of bismuth precipitation: *a* –  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ ; *b* – precipitate formed in the interaction of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with sodium salicylate solution at 70 °C for 1 h; *c* – bismuth (III) oxide salicylate; *d* – precipitated from nitrate solutions at 70 °C.

(IR), 1237 and 1250  $\text{cm}^{-1}$  (Raman), planar bending vibrations  $\delta(\text{CO-H})$  at 1345 (IR) and 1389  $\text{cm}^{-1}$  (Raman) in the spectrum of bismuth (III) oxide salicylate confirms the presence of non-dissociated phenol group in the coordinated salicylate anion.

In the IR spectrum of bismuth (III) oxide salicylate in the region 2950–3350  $\text{cm}^{-1}$ , broad absorption bands are observed with the maximum at 3060  $\text{cm}^{-1}$  related to the stretching vibrations of the ring  $\nu(\text{CH})$  and the maximum at 3200  $\text{cm}^{-1}$  related to the stretching vibrations of phenol groups that participate in the formation of the system of hydrogen bonds in the compound.

The electron microscopic images also provide evidence of partial and complete transformations in the  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ -solution system. The sample  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  (Fig. 5, a) exhibits elongated prismatic crystals 20–30  $\mu\text{m}$  long and 5–10  $\mu\text{m}$  wide. After the treatment of this compound with the sodium salicylate solution at the molar ratio of salicylate ions to bismuth  $n = 1.1$  for 1 h, needle-like crystals of bismuth (III) oxide salicylate are formed on the prismatic crystals of the initial solid compound; the length of the formed crystals is 10–20  $\mu\text{m}$  and their thickness is 0.2  $\mu\text{m}$  (see Fig. 5, b). The product of the treatment of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with the solution of salicylic acid at this molar ratio is composed of needle-like crystals of bismuth (III) oxide salicylate without visible crystals of the initial compound (see Fig. 5, c). Bismuth (III) oxide salicylate is precipitated from the nitric acid solutions within pH 0.9–3 at 70  $^{\circ}\text{C}$  also in the form of needle-like crystals (see Fig. 5, d) 1–5  $\mu\text{m}$  long and about 0.2  $\mu\text{m}$  thick.

The DTA data and the results of thermogravimetric (TG, DTG) analysis of the sample  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  (Fig. 6, a) in the air provide evidence of the sequential detachment of three water molecules (endo-effects at 125, 180 and 330  $^{\circ}\text{C}$ ). Then, with the removal of one water molecule from the internal sphere of the complex (endo-effect at 270  $^{\circ}\text{C}$ ), dehydroxylation process starts. The next five endo-effects at 330, 375, 440, 520 and 600  $^{\circ}\text{C}$  are connected with its completion and the destruction of five nitrate ions [8]. The endothermic effect at 720  $^{\circ}\text{C}$  is explained by polymorphous transformations of monoclinic  $\alpha$ -modification of  $\text{Bi}_2\text{O}_3$

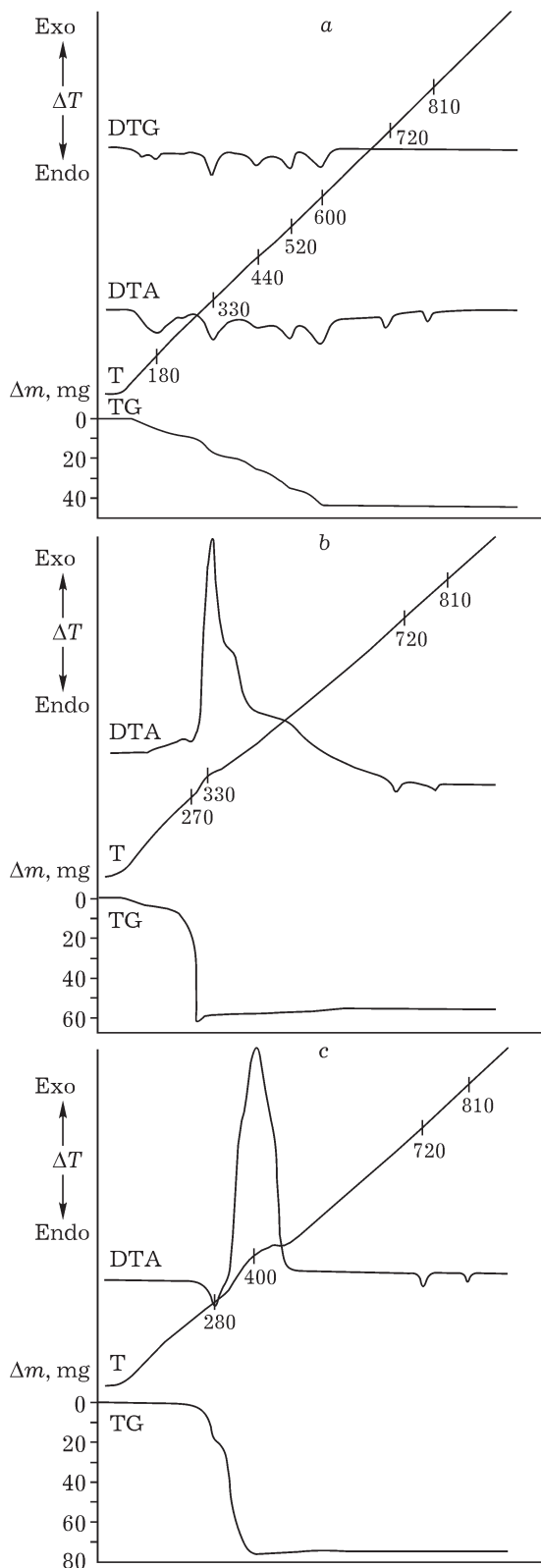


Fig. 6. Curves of thermal analysis of the products of bismuth precipitation in the air: a –  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ ; b – precipitate obtained in the interaction of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with sodium salicylate solution at 70  $^{\circ}\text{C}$  for 1 h; c – bismuth (III) oxide salicylate. Weighed portions of samples: 200 mg.

into the cubic face-centred high-temperature modification  $\delta\text{-Bi}_2\text{O}_3$  which is stable up to the melting point of the oxide at 824 °C (endo-effect in the region 810–850 °C) [20].

The thermogram of bismuth (III) oxide salicylate (see Fig. 6, c) shows that sample heating results in the formation of bismuth oxide. Thermal decomposition of bismuth (III) oxide salicylate starts with its melting (endothermic effect at 280 °C), subsequent decomposition of salicylate ions (exothermal effect at 400 °C), and the formation of bismuth oxide. According to the X-ray data [21], bismuth oxide obtained by thermal decomposition of bismuth (III) oxide salicylate for 6 h at a temperature of 300 °C corresponds to the tetragonal modification  $\beta\text{-Bi}_2\text{O}_3$  which is then transformed into the monoclinic  $\alpha\text{-Bi}_2\text{O}_3$  at a temperature of 350 °C and higher. The calculated mass loss (71.6 mg) connected with the decomposition of  $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)\text{O}$  into  $\text{Bi}_2\text{O}_3$  agrees with the detected value 71.3 mg. It should be noted that the decomposition of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  to bismuth oxide occurs at 600 °C, while its mixture with bismuth (III) oxide salicylate decomposes at substantially lower temperatures (see Fig. 6, b). This effect can be used in the synthesis of fine crystalline bismuth oxide powders because it allows one to carry the process out at low temperatures and avoid agglomeration of the product.

So, the following synthesis scheme may be proposed to obtain bismuth (III) oxide salicylate from metal bismuth of Vi 1 grade, which is usually used as the initial raw material for obtaining its compounds. Metal bismuth containing, %: bismuth 98.5, lead  $1.35 \cdot 10^{-2}$ , copper  $6.3 \cdot 10^{-3}$ , iron  $1.0 \cdot 10^{-3}$ , zinc  $5.6 \cdot 10^{-4}$  is preliminarily oxidized with atmospheric oxygen by adding 15 % of technical grade bismuth oxide to the melt under mixing, which allows one to decrease the consumption of nitric acid and to avoid the evolution of nitrogen oxides at the stage of obtaining the solutions of bismuth nitrate [22]. Technical grade bismuth oxide in the amount of 2.0 kg was treated under mixing with 4.3 L of  $\text{HNO}_3$  with the concentration of 7.0 mol/L.

According to the first version, 600 g of salicylic acid is added to 13.0 L of distilled water at a temperature of 23 °C and under mixing add 2.17 L of the aqueous solution of NaOH

with the concentration of 2.0 mol/L till complete dissolution of the crystals of salicylic acid (pH 7.0). Under mixing, 2.05 L of bismuth-containing solution with bismuth content 420 g/L and 2.1 L of NaOH solution with the concentration of 2.0 mol/L are added to the resulting solution. The molar ratio of salicylic acid to bismuth in the system  $n = 1.06$ , pH 1.6. The mixture is stirred for 30 min at a temperature of 23 °C, temperature is increased to 70 °C, and the mixture is stirred for 3 h more. Bismuth (III) oxide salicylate is washed two times with 20 L of distilled water heated to 60 °C, filtered and dried at a temperature of 90 °C for 6 h. The product is 1.48 kg of bismuth (III) oxide salicylate containing, %: bismuth 57.5, lead  $22 \cdot 10^{-3}$ , silver  $1.3 \cdot 10^{-3}$ , copper  $1.0 \cdot 10^{-4}$ , iron  $5.0 \cdot 10^{-4}$ , zinc  $1.2 \cdot 10^{-4}$ . Direct recovery of bismuth into the product is 99.2 %.

The second version of obtaining bismuth (III) oxide salicylate was carried out according to the reaction of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  interaction with the solution of salicylic acid. Bismuth was preliminarily purified from accompanying metals by adding  $(\text{NH}_4)_2\text{CO}_3$  solution with the concentration of 2.5 mol/L to 2.05 L of bismuth-containing solution with bismuth content of 420 g/L to pH 0.9 [23]. The precipitate was washed on the filter with distilled water and charged gradually into the solution containing 13.0 L of distilled water and 600 g of salicylic acid. The mixture was heated to 70 °C and mixed for 3 h. The precipitate was two times washed with 20 L of distilled water heated to 60 °C, filtered and dried at a temperature of 90 °C for 6 h. The product was 143 g of bismuth (III) oxide salicylate containing, %: bismuth 57.6, lead  $1.2 \cdot 10^{-4}$ , silver  $4.0 \cdot 10^{-6}$ , copper  $5.0 \cdot 10^{-6}$ , iron  $2.2 \cdot 10^{-4}$ , zinc  $3.6 \cdot 10^{-5}$ . Direct recovery of bismuth into the product is 95.6 %.

Larger-scale tests demonstrated that bismuth (III) oxide salicylate for use in medicine can be obtained either by precipitation from nitric solutions used in the production of its compounds or according to the reaction of the interaction of solid  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  with the solution of salicylic acid. The second method allows one to obtain the product more than an order of magnitude purer with respect to the metals accompanying bismuth.



## CONCLUSION

So, it is reasonable to carry out the synthesis of high-purity bismuth (III) oxide salicylate, for use as the medical substance of antiulcer and antidiarrheal preparations, from metal bismuth according to the following scheme: 1) oxidize metal bismuth preliminarily with atmospheric oxygen, 2) purify bismuth from accompanying metals by its precipitation from nitrate solutions in the form of trihydroxo-pentaoxo-hexabismuth (III) trihydrate, 3) transform it into bismuth (III) oxide salicylate by treatment with the aqueous solution of salicylic acid.

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