

UDC 542.65:66.093:661.887

## Preparation of Bismuth (III) Malates by Precipitation from Nitrate Solutions

E. V. TIMAKOVA<sup>1,2</sup>, L. I. AFONINA<sup>1,2</sup>, YU. I. YUKHIN<sup>1</sup>, N. V. BULINA<sup>1</sup>, and V. A. VOLODIN<sup>3, 4</sup><sup>1</sup>*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, Kemerovo, Russia**E-mail: timakova@solid.nsc.ru*<sup>2</sup>*Novosibirsk State Technical University, Novosibirsk, Russia*<sup>3</sup>*Rzhanov Institute of Semiconductor Physics, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia*<sup>4</sup>*Novosibirsk State University, Novosibirsk, Russia*

(Received April 6, 2016)

### Abstract

The precipitation of bismuth (III) from nitric acid solutions depending on the concentration of malate ions, process temperature, pH values of solutions upon the addition of an optically active *L*(-)-isomer and racemic *DL*-malic acid was studied by X-ray phase analysis (XPA) methods, IR and Raman scattering spectroscopy (RSS), thermogravimetry and chemical analysis. It was demonstrated that bismuth malate monohydrate with a composition of  $\text{BiC}_4\text{H}_3\text{O}_5 \cdot \text{H}_2\text{O}$  was precipitated when adding *L*(-)-malic acid into nitric acid solutions, and in case of the addition of *DL*-malic acid, a compound with a composition of  $\text{BiC}_4\text{H}_3\text{O}_5 \cdot 0.5\text{H}_2\text{O}$  is formed. Coordination of the bismuth cation with malic acid anions was studied by spectroscopic methods. It was found that malic acid residue in the compounds under study was thrice deprotonated, and their bond with the bismuth cations was carried out through all functional groups of malic acid. The conducted research of obtained bismuth malate demonstrated that *L*-malate samples in comparison with bismuth *DL*-malate were homogeneous by the particle size distribution, which does not require the additional cost on grinding the sample to a homogeneous state when using it as a medicinal substance, and an increase in process temperature allows obtaining more fine-grained powders. The advisability of the preparation of bismuth malate for medical purposes from bismuth metal was demonstrated with preliminary oxidation of the latter with air oxygen, dissolution of the resulting oxide in nitric acid (1 : 1) and precipitation of bismuth (III) malate by the addition of a bismuth-containing solution to a sodium malate solution with a molar ratio of malate ions to bismuth of 1.1–1.2 and process temperature of  $(60 \pm 10)^\circ\text{C}$ .

**Key words:** precipitation from solutions, *L*(-)-malic acid, *DL*-malic acid, bismuth (III) malate, X-ray phase analysis, IR and Raman spectra, thermal analysis

### INTRODUCTION

Bismuth salts with succinic and dihydroxy succinic (tartaric) acids are widely used for medical purposes. A basic salt of succinic acid is a drug substance of Biquinol (Merck, Ger-

many) and Pholcones (Cooper, France) preparations, used to treat tonsillitis, laryngitis and pharyngitis. Bismuth tartrate monohydrate of a composition of  $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$  is an active substance in the antisyphilitic drug Bysmoverol [1]. Therefore, bismuth salts with malic (hydroxy

succinic) acid are promising for the use in medical purposes at manufacturing antibacterial drugs. Malic acid is a metabolite of the Krebs cycle and its action on the organism is distinguished by a high physiologicity. Due to the presence of an asymmetric carbon atom, malic acid exists in two optically active [2] and racemic forms [3, 4], *L*(-)-malic acid is common in nature, it is contained in the acid fruits of gooseberries, rowan, in rhubarb, as calcium salt in tobacco, as well as in small amounts in wine [5].

To date, bismuth compounds with *L*(-)-malic acid have been considered only as models of interest to describe structures of bismuth salts used to treat chronic gastritis [6]. The structure of a salt obtained upon the interaction of equimolar amounts of bismuth nitrate pentahydrate and *L*(-)-malic acid was studied [7]. Upon aging of the system for several days, colourless, cubic monocrystals of  $C_4H_5BiO_6$  structure crystallized in a spatial group  $P3_121$ . It is also noted in [7] that the powdery product is precipitated with methanol from aqueous solutions.

The formation of various bismuth compounds with the optically active tartaric acid [1] promising for the use as antibacterial drugs obtained from solutions of mineral acids was earlier demonstrated by us. Until current systematic studies, regarding an opportunity to form bismuth compounds with malic acid obtained resulting from precipitation from bismuth solutions have not been carried out. Bismuth (III) compounds are usually synthesized by hydrolytic processing of bismuth solutions in nitric acid. Due to this, studying the precipitation process of bismuth malates is of practical interest.

With a view to obtaining bismuth compounds that can be used as medicinal substances, the present work presents the research results for the effect of the concentration of malate ions, process temperature and medium acidity for precipitation degree of bismuth and the composition of the resulting compounds upon the addition of optically active malic acid (*L*-form) and racemic *DL*-malic acid. Based on the studies conducted, an environmentally friendly method for the preparation of bismuth (III) malates directly from nitrate solutions of manufacturing bismuth compounds that is of practical interest was proposed.

## EXPERIMENTAL

Chemically pure or extra-pure mineral salts and alkalies were used in the work. The original solution of bismuth nitrate (400 g/L of bismuth, 100 g/L of free nitric acid) was prepared by dissolution of extra pure 13-3, respectively, in nitric acid with a concentration of 6 mol/L.

Hydrolytic precipitation of bismuth from nitrate solutions was carried out in fluoroplastic or glass vessels fitted with stirrers, thermostating of which was performed in WB-2 water basses. Precipitation of bismuth malates from nitric acid solutions was performed by the addition of a bismuth-containing solution to a solution of malic acid or sodium malate. The ratio of the volumes of the initial and final solutions was 1 : 10, the addition of distilled water corrected it. The mixture was stirred for 1 h. The precipitate was filtered off, rinsed with distilled water and dried in air.

To determine the phase composition of samples X-ray diffraction (XRD) method was used. The survey was conducted on a D8 Advance diffractometer (Bruker, Germany) in the geometry of Bragg-Brentano with characteristic  $CuK_{\alpha}$  radiation in an angle range of  $4^{\circ} < 2\theta < 70^{\circ}$  with a step of  $0.02^{\circ}$ . Phase analysis was performed using the PDF-2 database (ICDD).

Infrared adsorption spectra in the middle infrared ( $400-4000\text{ cm}^{-1}$ ) were recorded using a Scimitar FTS 2000 FTIR spectrometer (Digilab, the USA), samples were prepared as pellets with calcined KBr. Raman scattering spectra were recorded at room temperature in the backscattering geometry, a line of  $Ar^{+}$  laser with a wavelength of 514.5 nm was used for excitation, the signal from scattered light was analysed in polarization perpendicular to the incident light polarization geometry Z(XY)-Z. A Horiba JobinYvon T64000 spectrometer in a single operation mode (without pre-monochromator) was used.

Determination of macroamounts of Vi(III) in solutions was carried out by titration with a solution of complexon III with Xylenol Orange Indicator, microamounts were determined photocolometrically with sodium iodide [8]. The precipitation products were dissolved with heating in diluted  $HNO_3$  (1 : 1). The content of car-

bon, hydrogen and nitrogen in the samples synthesized was determined by the modified Pregl method. Analysis of impurity metals was performed by the atomic adsorption method using a Varian AA 280FS spectrophotometer (Australia).

The concentration of free hydrogen ions in solutions was determined by titration with caustic soda solution with preliminary masking of bismuth cations by complexon III with methyl red indicator [9].

Thermal analysis of samples was carried out using an STA 449 F1 Jupiter thermoanalytical complex (Netzsch, Germany) in the dynamic mode with heating in various atmospheres Ar/O<sub>2</sub> (80/20; O<sub>2</sub> 10 mL/min; Ar 40 mL/min). Sample weights of 180–200 mg was placed in crucibles of Pt–10 % Rh alloy and heated with a rate of 10 °C/min to 500 °C.

Scanning electron microscopy (SEM) was carried out using Hitachi TM 1000 scanning electron microscope (Hitachi Ltd., Japan).

## RESULTS AND DISCUSSION

Studies on precipitation of bismuth malates from nitric acid solutions at a temperature of

(23±2) and (60±2) °C and the addition of racemic *DL*-malic acid and optically active malic acid (*L*-form) indicate that the bismuth precipitation degree (*R*) depends on the introduced amount of malate ions and process temperature. The degree increases with a rise of the concentration of malate ions and process temperature. With the molar ratio of *DL*-malate ions to bismuth in a solution (*n*) of 1.0, *R* is 79.7 and 85.7 % for temperatures of (23±2) and (60±2) °C, respectively. With increasing *n* up to 3.0, *R* increases to 95.7 and 92.6 %, respectively.

According to X-ray phase analysis, nitrates with the composition [Bi<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>](NO<sub>3</sub>)<sub>6</sub>·4H<sub>2</sub>O and [Bi<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>](NO<sub>3</sub>)<sub>6</sub>·H<sub>2</sub>O, respectively, are formed in the absence of malate ions in the system at 23 и 60 °C [10]. Diffraction maxima indicating the formation of a new compound in the system appear clearly in roentgenograms of the resulting precipitates at *n* of 0.25 и 0.5 (Fig. 1, curve 1). Maxima typical for free *DL*-malic acid (ICDD 46-1864) were not detected. Roentgenograms of samples obtained with *n* = 1 correspond to *DL*-bismuth malate (see Fig. 1, curve 2), the literature data regarding the preparation of this compound have not been found by us. Herewith, the data of chemical analysis

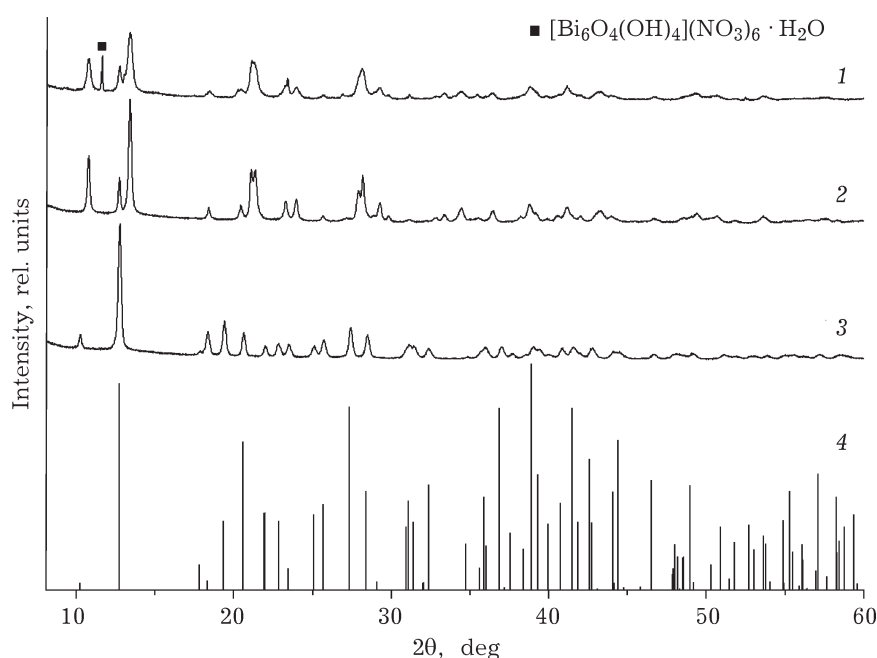


Fig. 1. Roentgenograms of the products of precipitation of Bi(III) from nitric acid solutions upon the addition of *DL*-malic (1, 2) and *L*(-)-malic (3) acids with a molar ratio of malate ions to bismuth *n* of 0.5 (1) and 1 (2, 3) and dash spectrum for *L*(-)-bismuth malate (4), modelled based on the data of [7]; temperature of 60 °C.

for these samples (58.5 % Bi, 13.79 % C, 1.12 % H) indicate that the molar ratio of Bi(III) to malate ions is 1 : 1. Based on the data of thermal analysis given further, the composition of the compound to be deposited can be represented as  $\text{BiC}_4\text{H}_3\text{O}_6 \cdot 0.5\text{H}_2\text{O}$ . Precipitation of a compound with the indicated composition is observed with a further increase in the molar ratio of malate ions to bismuth in a system up to 3 and more. Resulting from multiple water flushing, according to X-ray phase analysis, the compound composition is not changed.

X-ray phase analysis of samples obtained upon the addition of *L*(-)-malic acid into nitric acid solutions at 60 °C demonstrated that beginning with *n* of 0.5, diffraction maxima (see Fig. 1, curves 3, 4), typical for bismuth malate monohydrate with the composition of  $\text{C}_4\text{H}_3\text{O}_5\text{Bi} \cdot \text{H}_2\text{O}$  appear in diffractograms of the precipitation products [7]. Diffraction maxima typical for free *L*(-)-malic acid (ICDD 42-1702) are not observed. The bismuth content of 1.0 in the resulting precipitate is 57.6 % (calculated 58.4), C 12.68 % (calculated 13.41), H 1.29 (calculated 1.40). The bismuth extraction degree into a precipitate is 59.8 % and it is not increased at a further increase in the concentration of malate ions in a system, and according to XPA,  $\text{C}_4\text{H}_3\text{O}_5\text{Bi} \cdot \text{H}_2\text{O}$  is also formed. Washing the precipitate with water does not change its composition.

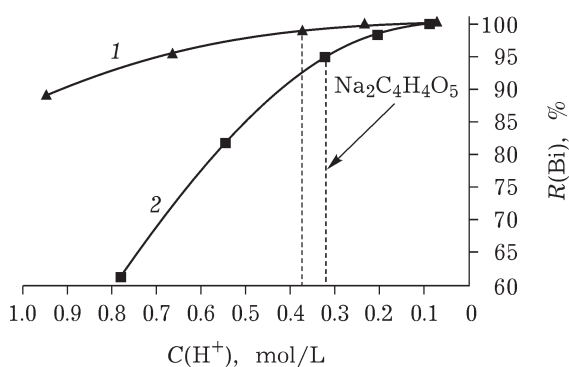


Fig. 2. Degree of Bi(III) precipitation ( $R$ , %) vs. free acidity of a solution upon the addition of *DL*- (1) and *L*(-)-malic (2) acids to a nitrate acid bismuth-containing solution. The molar ratio of malate ions to bismuth Bi(III)  $n = 1.1$ ; process temperature is 60 °C; the dotted line shows the value of solution acidity corresponding to the neutralization of malic acid into neutral sodium salt.

The bismuth precipitation degree from nitric acid solutions of *L*(-)-malic acid at 23 °C does not exceed 40.8 % with all the studied values of *n*. The data of X-ray phase and chemical analysis testify the formation of bismuth *L*(-)-malate with the composition  $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ .

To obtain the target product with a sufficient degree of its extraction into a precipitate the study of the effect of the medium acidity for the precipitation degree of bismuth *DL*- and *L*(-)-malates from nitric acid solutions (Fig. 2). The studies were carried out at the constant ratio of malate ions to bismuth in solution *n* of 1.1 with process temperature of 60 °C by the addition of various amounts of sodium hydroxide (the first point of the dependence correspond to solutions without the addition of alkali). The carried out studies demonstrated that with decreasing the solution acidity, the bismuth precipitation degree is 99.0 and 95.0 % for bismuth *DL*- and *L*(-)-malates, correspondingly (curve 2), the free acidity of solutions is 0.37 and 0.32 M and corresponds to malic acid neutralization to neutral sodium salt. The degree of bismuth extraction into a precipitate upon the addition of sodium hydroxide up to the solution acidity of 0.07 and 0.086 M is quantitative and amounts to 99.9 and 99.8 %, respectively. According to the data of X-ray phase and chemical analysis, bismuth *DL*-malate with the composition  $\text{C}_4\text{H}_3\text{O}_5\text{Bi} \cdot 0.5\text{H}_2\text{O}$  is the precipitation product in the whole range of the studied values of solutions acidity in case of the addition of *DL*-malic acid and bismuth *L*(-)-malate with the composition  $\text{C}_4\text{H}_3\text{O}_5\text{Bi} \cdot \text{H}_2\text{O}$  is precipitated upon the addition of *L*(-)-malic acid.

The presence of water in the composition of the studied salts is also confirmed by the data of thermal analysis (Fig. 3, *a* and *b*). The nature of TG curves (see Fig. 3 *a* and *b*, curves 1) may be driven by the removal of crystallized water molecules (endo effect with a maximum at 100 (a) and 80 °C (b)) followed by decomposition of the compounds with the exo effect at DTA curves with a maximum at 290 °C (a) and 310 °C (b) (see Fig. 3, curves 3), associated, according to mass spectrometry, with the release of water and  $\text{CO}_2$  resulting from the decomposition of malate ions. Subsequent minor exo effects at ~375 °C are related to the transition of a  $\beta\text{-Bi}_2\text{O}_3$  tetragonal modification into monoclinic  $\alpha\text{-Bi}_2\text{O}_3$ .

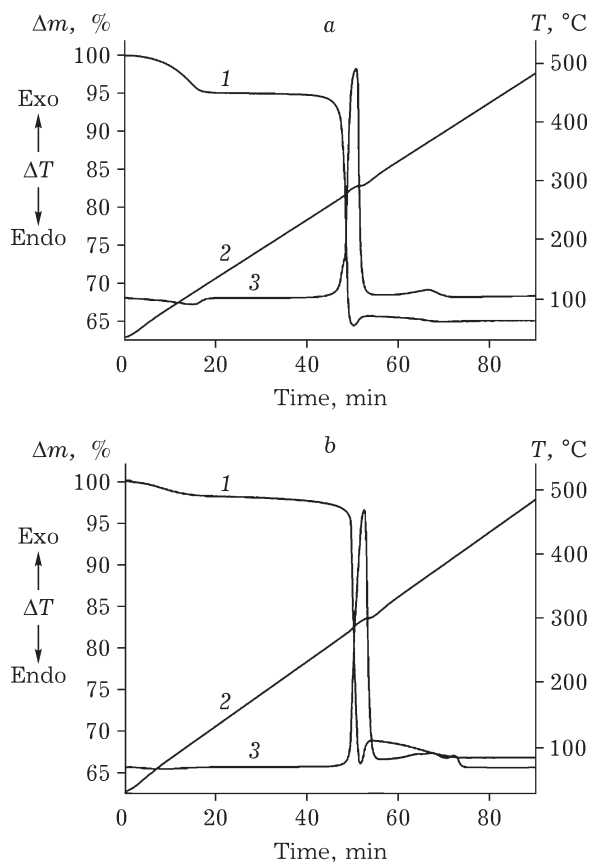


Fig. 3. Thermal analysis curves of neutral *L*-bismuth malate (a) and *DL*-bismuth malate (b) in air: TG (1), temperature (2), differential scanning calorimetry (DSC) (3).

The mass loss at the first decomposition stage of bismuth *L*(-)-malate is 5.0 % (calculated 5.03 %) (see Fig. 3, a, curve 1) resulting from the water removal, according to the determined composition  $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ . The mass loss for *DL*-bismuth malate is lower at the first stage and amounts to 2.50 % (calculated 2.58 %), which indicates the removal of twice lower number of water molecules, corresponding to the proposed composition  $\text{BiC}_4\text{H}_3\text{O}_6 \cdot 0.5\text{H}_2\text{O}$ . The total mass loss is 35.0 % (calculated 35.1 %) for *L*(-)- and 33.5 % (calculated 33.2 %) for bismuth *DL*-malate, which corresponds to the formation of bismuth oxide with the composition  $\text{Bi}_2\text{O}_3$ . Thus, the data of thermal analysis indicate an opportunity of drying bismuth malates at temperatures of 60–70 °C without a change in compound composition.

According to the results of X-ray structural analysis (XSA), presented in work [7], bismuth in the structure of *L*(-)-bismuth malate with

the composition  $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$  is chelated by four triply deprotonated residues of malic acid in various ways, forming five-membered, six-membered and two four-membered rings. The oxygen atom of crystallization water molecules is also included into the coordination sphere with total coordination number 9. The data of IR and Raman scattering spectroscopy (RSS) are consistent with XSA data. Figure 4 presents spectra of the resulting bismuth salts in comparison with the corresponding malic acids. The main characteristic vibrational bands for malic acids later disappearing in IR and Raman spectra of their bismuth salts are given in Table 1. Observed changes in spectra of salts, in comparison with spectra of acids point out at the presence of triply deprotonated residues of malic

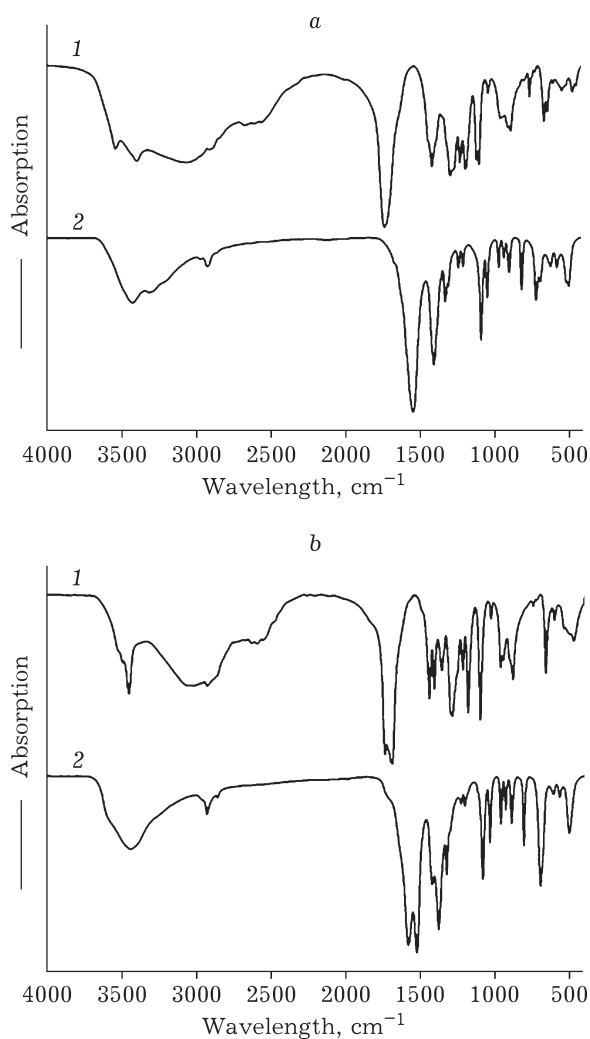


Fig. 4. IR absorption spectra of malic acid (1) and bismuth salts (2) upon the addition of *L*(-)- (a) and *DL*-malic acid (b) to nitric acid solutions.

TABLE 1  
Characteristic vibrational bands in IR and Raman spectra of malic acid

<i>L</i> (-)-malic acid		<i>DL</i> -malic acid		Band assignment
IR	Raman	IR	Raman	
3536 weak	3540 weak	3490 weak sh.	3495 very weak	$\nu(\text{OH})_{\text{CHOH}}$
3392 weak	3393 weak	3447 m.	3446 weak	
3070 wide weak	3100 weak	3015 wide sh.		$\nu(\text{OH})_{\text{COOH}}$ included in hydrogen bonds
2668 weak		2667 weak		Dimers bound by hydrogen bonds
2600–2500				
1732 v. s.	Inactive	1739 s.	Inactive	$\nu(\text{C}=\text{O})$ of dimers of carboxyl groups
	IR	1716 s.	Raman	out of plane [12]
		1700 s.		
		1689 v. s.		
Inactive	1655 s.	Inactive	1679 s.	$\nu(\text{C}=\text{O})$ of dimers of carboxyl groups
IR		IR	1636 s.	in plane [12]
1440 sh.	1444 m.	1443 m.	1451 m.	Compound vibrations $\nu(\text{C}-\text{O}) + \delta(\text{OH})_{\text{COOH}}$
1291 m.	1292 sh.	1289 wide s.	1298 weak	$\delta(\text{OH}) + \nu(\text{C}-\text{O})_{\text{COOH}}$
1278 weak	1282 sh.	1277 sh.	1280 weak	$\delta_{\tau}(\text{CH}_2)$ , $\delta(\text{OH})$ , $\nu(\text{C}-\text{O})$
1269 m.	1269 weak	1267 sh.	1263 weak	$\delta(\text{CH})_{\text{CHOH}}$
1115 m.	1119 weak	1103 s.	1100 m.	$\delta_{\text{s}}(\text{CH}_2)$ , $\nu(\text{C}-\text{O})$ , $\delta(\text{OH})$
1098 m.	1100 m.			
956 m. sh.	960 m.	968 m.	967 s.	$\nu(\text{C}-\text{C})$ , $\delta_{\gamma}(\text{C}-\text{O})$
	969 m. sh.			

Note.  $\nu$  is stretching vibration;  $\delta$  is flat deformation vibration;  $\delta_{\tau}$  is torsional vibration;  $\delta_{\text{s}}$  is scissor vibration;  $\delta_{\gamma}$  is non-planar deformation vibrations (torsional); s. is strong; v. s. is very strong; m. – medium, sh. – shoulder.

acids and binding a bismuth-containing cation with all functional groups of malic acid. These findings are also confirmed by the appearance characteristic bands for salts in IR spectra. Thus, bands of asymmetric  $\nu_{\text{as}}(\text{COO}^-)$  stretching vibrations of carboxylate groups with a maximum at 1539 and 1549  $\text{cm}^{-1}$  and symmetric  $\nu_{\text{s}}(\text{COO}^-)$  stretching vibrations of carboxylate groups at 1400 and 1413  $\text{cm}^{-1}$  that also testify substitution of protons in the carboxyl group of carboxylic acids by a Bi-containing cation appear in IR spectra of bismuth *DL*-malates (see Fig. 4, *a*, curve 2). Bands with wave numbers of 1583, 1526  $\text{cm}^{-1}$  and 1425, 1381  $\text{cm}^{-1}$ , respectively, in IR spectra of *DL*-bismuth malates (see Fig. 4, *b*, curve 2) correspond to stretching vibrations of carboxylate groups  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$ . Bending vibration bands of carboxylate groups appear as medium intensity bands at 812  $\text{cm}^{-1}$  (see Fig. 4, *a*, curve 2) and 811  $\text{cm}^{-1}$  (see Fig. 4, *b*, curve 2) [13]. Additionally, stretching vibrations

of the Bi–O bond is observed as a medium intensity band with two maxima at 511 and 496  $\text{cm}^{-1}$  (see Fig. 4, *a*, curve 2) and a band at 509  $\text{cm}^{-1}$  (see Fig. 4, *b*, curve 2). The presence of water molecules in the compounds under study is indicated by broad bands with medium intensity of stretching vibrations of bands  $\nu(\text{O}-\text{H})$  of water in IR spectra of salts with maxima at  $\sim 3400$   $\text{cm}^{-1}$ , weak bands at 1668  $\text{cm}^{-1}$  (see Fig. 4, *a*, curve 2) and 1725  $\text{cm}^{-1}$  (see Fig. 4, *b*, curve 2) correspond to bending vibrations of water molecules [13]. Similar changes are observed in Raman spectra of the resulting salts.

Electron microscope images indicate that *L*-bismuth malate samples obtained upon precipitation of bismuth (III) from nitric acid solutions 60 °C by the addition of *L*(-)-malic acid with a concentration of a free acid in a solution of 0.55 M (without the addition of sodium hydroxide) represent aggregates with a size of 30–50  $\mu\text{m}$ , consisting of crystals with a size of 3–

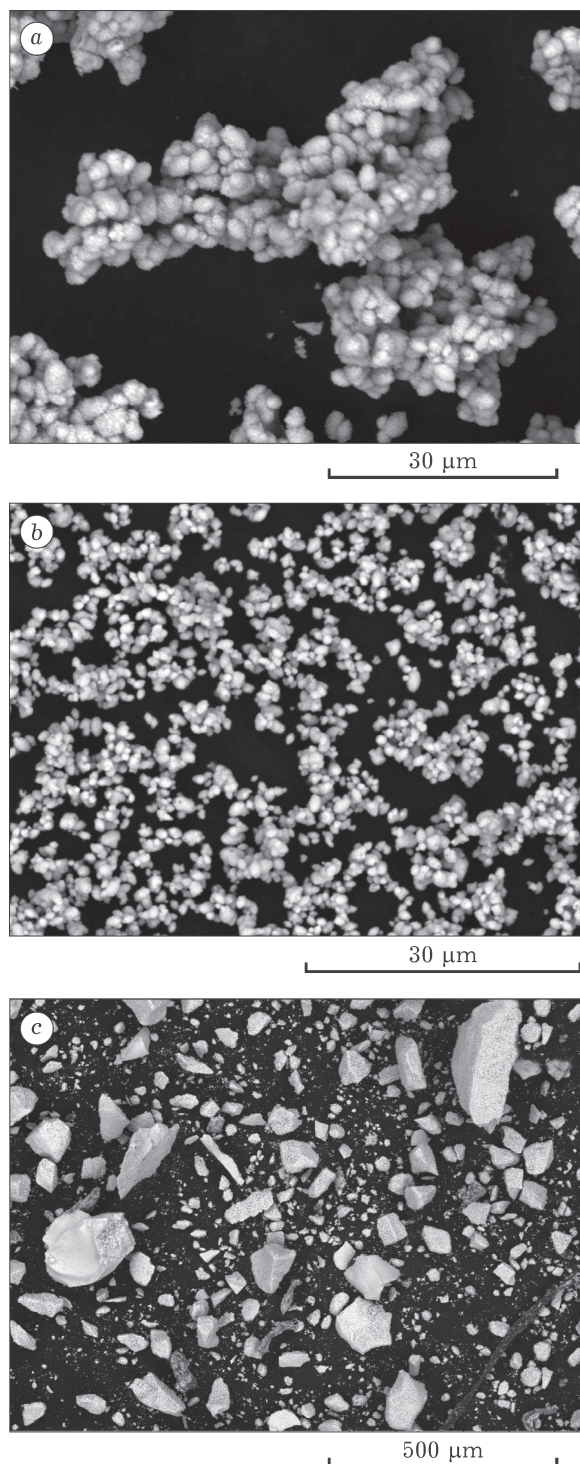


Fig. 5. Photomicrographs of *L*- (a, b) and bismuth *DL*-malate (c) obtained by precipitation from nitric acid solutions at process temperature of 23 (a, c) and 60 °C (b) with the addition of malic acid (a, c) and its sodium salt (b).

5 μm (Fig. 5, a). *L*-bismuth malate samples obtained at process temperature of 60 °C and solution acidity of 0.32 M (with neutralization of malic acid with sodium hydroxide to neutral

sodium salt) represent small cubic crystals with a size of 1–2 μm (see Fig. 5, b). When air drying *L*-bismuth malate samples represent white powders, while a glass-like white-coloured substance is formed upon drying *DL*-bismuth malates. When its grinding, crystals of the irregular shape and various morphology (see Fig. 5, c) or powders are formed depending on the degree of physical impact. Herewith, the concentration of a free acid in a solution does not affect the product morphology. Additionally, chemical analysis data demonstrated that bismuth *L*-malate samples obtained without alkalization of solution, as well as bismuth *DL*-malates obtained with any solution acidity contain ~0.4 % nitrogen, which is ~2 %, recalculating for the content of nitrate ions. This demonstrates bismuth coprecipitation as oxo-hydroxy-nitrate or capture of nitrate ions from solutions, which is related to the morphological peculiarities of the resulting products. The conducted researches demonstrated that *L*-bismuth malate samples obtained at a temperature of 60 °C and solution alkalization were homogeneous by particle size distribution, which does not require additional costs for sample grinding to the homogeneous state upon its use as a medicinal substance, as well as the content of nitrate ions in these samples does not exceed 0.01 %, according to chemical analysis data. Thus, given that malic acid in living organisms is present precisely in the *L*(-)-form, bismuth *L*-malate samples precipitated from nitric acid solutions are morphologically homogeneous and better correspond to the requirements of purity for medicinal substances, it is they that are most promising as a substance to prepare antibacterial bismuth drugs in comparison with *DL*-bismuth malates. In view of the above, fine crystalline powders of bismuth *L*-malate should be obtained by precipitation from nitric acid solutions of bismuth *via* the addition of a solution of neutral sodium malate at process temperature of (60±10) °C.

An environmentally safe method of the preparation of bismuth tribenzoate, at which bismuth oxide is used to prepare nitric acid solutions of bismuth, was proposed by us earlier [14]. A nitric acid solution of bismuth (420 g/L, 62 g/L of free nitric acid) prepared by the described method [14] was added to a solution of

neutral sodium malate (the preparation of the solution was performed by neutralization of *L*(-)-malic acid with a sodium hydroxide solution, the molar ratio of malate ions to bismuth *n* was 1.1). The mixture was heated to 60 °C, stirred for 1 h and let stand. The mother solution was separated by decantation; the precipitate was washed twice with distilled water. The product was dried at a temperature of 70 °C for 6 h. The resulting *L*-bismuth malate (III) had the following composition (mass fraction, %): Bi 36.51, Pb  $5.0 \cdot 10^{-4}$ , Cu  $2.0 \cdot 10^{-6}$ , Ag  $3.0 \cdot 10^{-6}$ , Fe  $1.0 \cdot 10^{-4}$ , Zn  $3.0 \cdot 10^{-5}$ , Cd  $6.0 \cdot 10^{-6}$ . The yield of bismuth into the final product was 94.8 %.

## CONCLUSION

Thus, in case of the addition of *L*(-)-malic acid, bismuth is precipitated from nitric acid solutions with a molar ratio of malate ions to bismuth in solution (*n*) of 0.25–3.0 and a temperature of 23–60 °C as bismuth malate monohydrate with the composition  $\text{BiC}_4\text{H}_3\text{O}_5 \cdot \text{H}_2\text{O}$  of the known crystalline structure, and when adding *DL*-malic acid, as neutral salt with the composition  $\text{BiC}_4\text{H}_3\text{O}_5 \cdot 0.5\text{H}_2\text{O}$ . It was demonstrated that bismuth malates were advisable to obtain by preliminary oxidation of metal bismuth with air oxygen, dissolution of the resulting bismuth oxide in nitric acid, the addition of the resulting nitric acid solution of bismuth to a solution of neutral sodium malate with a molar ratio of malate ions to bismuth of 1.0–1.2 and process temperature of  $(60 \pm 10)$  °C. The advan-

tage of the suggested method is the preparation of bismuth *L*-malate directly from nitric acid solutions of manufacturing its compounds by bypassing the stage of using expensive neutral bismuth nitrate as a precursor. The method is environmentally safe, since emission into the atmosphere of toxic nitrogen oxides is avoided at the preparation stage of nitric acid solutions.

## REFERENCES

- 1 Timakova E. V., Logutenko O. A., Evseenko V. I., Mikhailova A. S., Yukhin Yu. M., *Khim Ust. Razv.*, 23, 1 (2015) 379.
- 2 Sluis P. van der, Kroon J., *Acta Cryst.*, C45 (1989) 1406.
- 3 Loock J. F. J. van, Havere W. van, Lenstra A. T. H., *Bull. Soc. Chim. Belg.*, 90 (1981) 161.
- 4 Van der Sluis P., Kroon J., *Acta Cryst.*, C41 (1985) 956.
- 5 Zefirov N. S., Kulov N. N., Zolotov Yu. A., Kabanov V. A., Kalechits I. V., Kolotykin Ya. M., Koptuyug V. A., Kutepov M. A., Malyusov V. A., Nefedov O. M., Talrose V. L., Spirin A. S., Stepanov N. F., Sholle V. D., Yagodin G. D. (Eds.), *Khimicheskaya Entsiklopediya*, vol. 5, Moscow, 1998.
- 6 Briand G.G., Burford N., *Chem. Rev.*, 99 (1999) 2601.
- 7 Herrmann W. A., Herdtweck E., Scherer W., Kiprof P., Pajdla L., *Chem. Ber.*, 126 (1993) 51.
- 8 Korostylev P. P., *Fotometricheskii i Kompleksometricheskii Analiz v Metallurgii* (Handbook), in A. I. Busev (Ed.), *Metallurgiya*, Moscow, 1984.
- 9 Polyak E. A., Musikhin R. N., Rodionova L. A., *Zh. Anal. Khim.*, 25, 12 (1970) 2447.
- 10 Yukhin Yu. M., Mikhailov Yu. I., *Khimiya Vismutovykh Soyedineniy i Materialov*, Izd-vo SO RAN, Novosibirsk, 2001.
- 11 Baranska H., Kuduk-Jaworska J., Szostak R., Romaniewska A., *J. Raman Spectrosc.*, 34 (2003) 68.
- 12 Max J.-J., Chapados C., *J. Phys. Chem.*, 108 (2004) 3324.
- 13 Kolandaivel P., Selvasekarapandian S., *Cryst. Res. Technol.* 28, 5 (1993) 665.
- 14 Timakova E. V., Udalova T. A., Yukhin Yu. M., *Chem. Sust. Dev.*, 18, 1 (2010) 79.

URL: <http://www.sibran.ru/en/journals/KhUR>