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Obtaining Bismuth-Potassium Citrate

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Abstract

The interaction of bismuth (III) citrate $\text{BiC}_6\text{H}_5\text{O}_7$ with the aqueous solutions of potassium hydroxide in different concentrations was studied by means of X-ray phase analysis, IR spectroscopy, thermogravimetry and chemical analysis. The conditions for the formation of the potassium salt of bismuth (III) citrate having the composition $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot \text{H}_2\text{O}$ were determined. Reasonability of obtaining this compound through the interaction of the aqueous solution of potassium hydroxide with bismuth (III) citrate with their molar and mass ratio equal to 1.0 was shown.

Key words: bismuth-potassium citrate, synthesis, aqueous solutions

INTRODUCTION

Bismuth compounds are used in medicine for more than two centuries as astringent, obduding and antiacid agents, and as the means to treat infections [1–3]. Drugs based on bismuth-potassium citrate are winning wide application during the recent years to treat the diseases of gastrointestinal tract [1].

It was demonstrated [4] that the compound with the composition $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$ gets crystallized at 8 °C from the aqueous solution of bismuth tripotassium dicitrate which is used to treat gastrointestinal tract. The crystal structure of this compound was determined. The interaction of bismuth nitrate with potassium citrate in water-glycerol (33.3 vol. %) solutions was studied in [5, 6]; it was shown that for the molar ratio of citrate ions to bismuth $n = 6$ in the system, the compound with the composition $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot 2\text{H}_2\text{O}$ is crystallized from solution during evaporation [5]. For $n = 8$, a compound with the composition $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot 3.5\text{H}_2\text{O}$ is crystallized from solution [6]. The authors of [5, 6] stress that for $n = 1.5$ the compound with the composition $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot (1.0–1.5)\text{H}_2\text{O}$ can

also be formed. It should be noted that the use of water-glycerol solutions for obtaining bismuth-potassium citrate requires complicated purification of the product from glycerol and is characterized by increased (1.5–8 times) consumption of potassium citrate. Because of this, the search for easier methods to obtain bismuth-potassium citrate is urgent.

In the present work we studied the process of obtaining bismuth-potassium citrate through the interaction of bismuth (III) citrate with the aqueous solutions of potassium hydroxide in different concentrations.

EXPERIMENTAL

Bismuth citrate with bismuth and citrate ion content 50.55 and 44.52 mass %, respectively, was obtained by dissolving bismuth oxide in nitric acid, followed by its deposition from bismuth-containing solution by adding the aqueous solution of citric acid at the process temperature of 60 °C according to the procedure reported in [7]. Bismuth oxide of os. ch. 13-3 reagent grade (TU 6-09-1853-77), nitric acid

of os. ch. 27-5 reagent grade GOST 11125-84), potassium hydroxide of kh. ch. reagent grade (GOST 24363-80), citric acid of kh. ch. reagent grade (GOST 3652-69) were used. The synthesis was carried out by treating a weighted portion of bismuth (III) citrate (20 g) with the aqueous solutions of potassium hydroxide (200 mL) of different concentrations (from 0 to 2 mol/L) under mixing for 4 h at temperature of (25 ± 2) and (70 ± 2) °C. The resulting product was separated by filtering and dried in the air. Bismuth content in solutions and reaction products was determined by means of photocolormetry in the presence of KI using KFK-2 instrument, after their preliminary dissolution in nitric acid (1 : 1). Citrate ion content was determined by means of permanganatometric titration [8] of solutions obtained after preliminary treatment of reaction products with the solution of 2M NaOH at 70–90 °C. X-ray phase analysis (XPA) of reaction products was carried out with the powder diffractometer Bruker ($\text{CuK}\alpha$ radiation, counter rotation rate 0.1 deg/min). The curves of differential thermal analysis (DTA), mass changes (TG) and the data on water content in the samples were obtained with the help of the instrument for synchronous thermal analysis STA 449F1 Jupiter (Netzsch, Germany) in helium flow with 25 vol. % O_2 50 mL/min, under heating up to 350 °C with heating rate 3 °C/min. Crucibles were made of Pt-10 % Rh alloy. The composition of gaseous products of thermolysis was analysed on a QMS 403 C Aëlos® quadrupole mass spectrometer conjugated with the

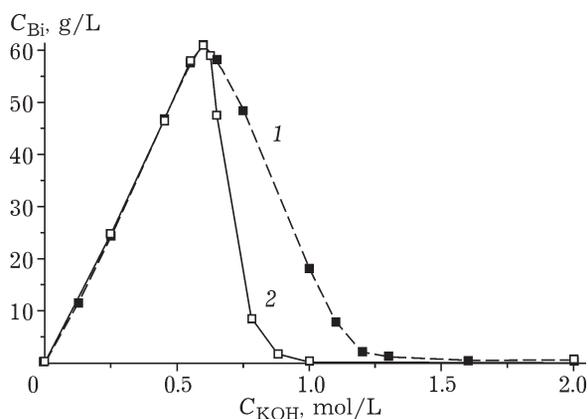


Fig. 1. Dependence of bismuth concentration in solution on the initial concentration of potassium hydroxide. Temperature (°C): 22 (1), 70 (2).

instrument. Absorption spectra in the IR region ($400\text{--}4000\text{ cm}^{-1}$) were recorded with a Specord 75 IR spectrophotometer. The samples were pressed in tablets with annealed KBr.

RESULTS AND DISCUSSION

Investigation of the interaction of bismuth (III) citrate $\text{BiC}_6\text{H}_5\text{O}_7$ with the aqueous solutions of potassium hydroxide at temperatures (25 ± 2) and (70 ± 2) °C showed (Fig. 1) that the dependence $C_{\text{Bi}^{3+}}\text{--}C_{\text{KOH}}$ passes through a maximum with an increase in the concentration of potassium hydroxide. Bismuth concentration in solution reaches 61.0 g/L for KOH solution concentration 0.6 mol/L; with further increase in the concentration of initial KOH solution the concentration of bismuth ions in solution decreases sharply.

According to XPA data (Fig. 2), with an increase in the concentration of potassium hydroxide and corresponding increase in bismuth

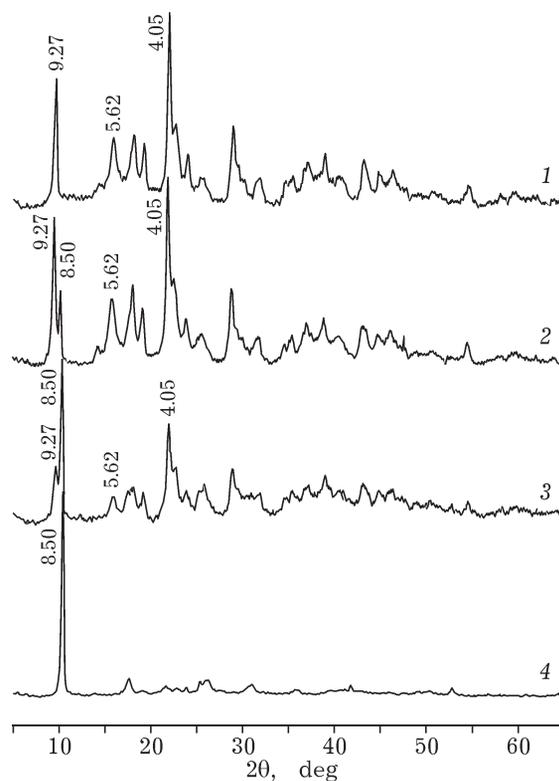


Fig. 2. Diffraction patterns of the samples of initial $\text{BiC}_6\text{H}_5\text{O}_7$ (1) and the products of its interaction with the aqueous solutions of potassium hydroxide (2–4). Concentration of KOH solution (mol/L): 0.1 (2), 0.2 (3), 0.4 (4).

ion concentration in solution, the intensities of diffraction maxima with d/n values equal to 9.27, 5.62 and 4.05 Å characteristic of $\text{BiC}_6\text{H}_5\text{O}_7$ compound decrease. The positions of these maxima remain almost unchanged, while for $C_{\text{KOH}} \geq 0.1$ mol/L an additional maximum of bismuth-potassium citrate clearly appears in the diffraction patterns at $d/n = 8.50$ Å ($T = (25 \pm 2)$ °C) (see Fig. 2, curve 2). The intensity of this peak increases with an increase in the concentration of potassium hydroxide solution, while the intensities of the diffraction maxima of $\text{BiC}_6\text{H}_5\text{O}_7$ decrease. For $C_{\text{KOH}} = 0.1$ –0.25 mol/L, the diffraction patterns of the products contain the peaks corresponding to the mixture of bismuth citrate and bismuth-potassium citrate. With an increase in the concentration of potassium hydroxide solution above 0.25 mol/L, the product has the following composition (%): K 7.37, Bi 41.99, Cit^{3-} (citrate ions) 35.0, H_2O 4.0. The molar ratio citrate ions/bismuth/potassium/water in the product is equal to 1 : 1 : 1 : 1, which corresponds to the composition $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot \text{H}_2\text{O}$. An increase in the concentration of potassium hydroxide solution above 0.7 mol/L causes a decrease in bismuth content in solution and amorphization of the product. The molar ratio of citrate ions to bismuth in

reaction product decreases, so for the concentration of potassium hydroxide solution equal to 0.75 mol/L, at a temperature of 70 °C, $n = 0.5$. Bismuth (III) oxide is formed as a result of further increase in KOH concentration (>1 mol/L). Temperature rise promotes the formation of bismuth oxide at lower KOH concentrations (≥ 1.0 mol/L).

To interpret the IR absorption spectrum of bismuth-potassium citrate (Fig. 3, curve 1), we used the spectra of citric acid (curve 3) and bismuth (III) citrate (curve 2) for reference. Band assignment was carried out according to the data reported in [9].

In the IR spectrum of bismuth-potassium citrate (see Fig. 3, curve 1), in comparison with the spectrum of citric acid, we observed the disappearance of the characteristic bands of carbonyl absorption (1745, 1708 and 1429 cm^{-1}) (see Fig. 3, curve 3). Instead, the bands of stretching symmetric and asymmetric vibrations of COO^- groups appear (1607 and 1439, 1379 cm^{-1}), which is the evidence of deprotonation of the carboxylic groups of citric acid [9]. The difference between the wavenumbers of symmetric (1439, 1379 cm^{-1}) and asymmetric (1607 cm^{-1}) stretching vibrations $\Delta(\nu_{\text{as}} - \nu_{\text{s}})\text{COO}^-$ reaches about 225 cm^{-1} . This is likely due to the fact that carboxylate groups of citrate residue are coordinated to bismuth mainly according to the monodentate type [10, 11]. Several overlapping absorption bands that are observed in the region 3500–3200 cm^{-1} can be assigned to the stretching vibrations of OH groups in water molecules. A broad range of band overlap in this region is the evidence of the large number of hydrogen bonds of different kinds. The absence of intense narrow absorption band that is observed in the IR spectrum of bismuth citrate (see Fig. 3, curve 2) around 3450 cm^{-1} ($\nu(\text{OH})_{\text{free}}$) can be the evidence of the participation of the free hydroxyl group of citrate residue in coordination with metal atoms [12, 13].

It follows from the data of thermal analysis that the appearance of TG curve of bismuth citrate (Fig. 4) may be due to the removal of one water molecule (endothermic effect at 135 °C) and subsequent decomposition of the compound with two exo effects at DTA curve at 278 and 288 °C, connected (according to the data of mass spectrometry) with the evolution

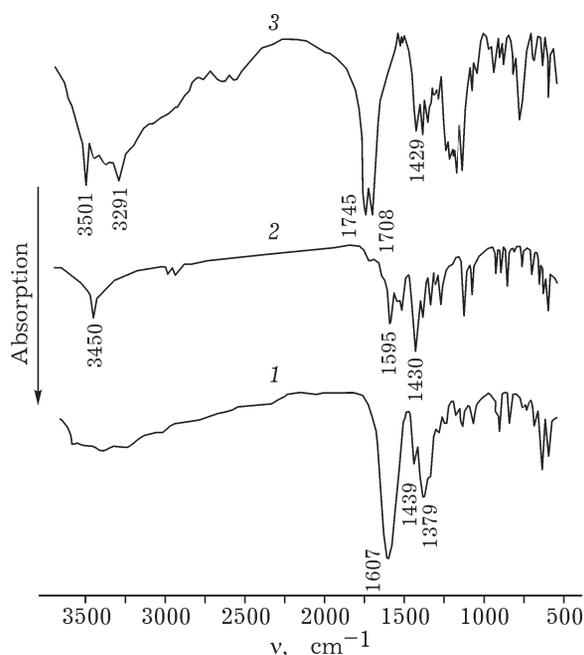


Fig. 3. IR spectra of $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot \text{H}_2\text{O}$ (1), $\text{BiC}_6\text{H}_5\text{O}_7$ (2), $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (3).

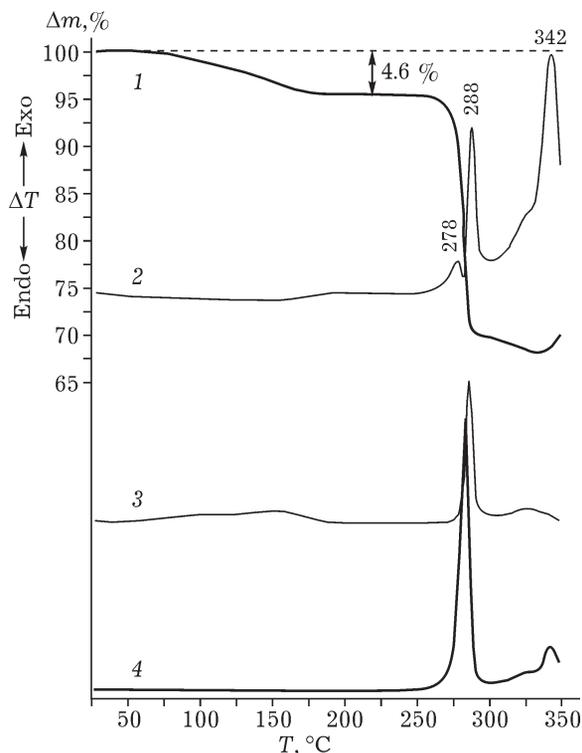


Fig. 4. Curves of thermal analysis of bismuth-potassium citrate sample: TG (1), DTA (2). Recorded masses: 18, H₂O (3); 44, CO₂ (4).

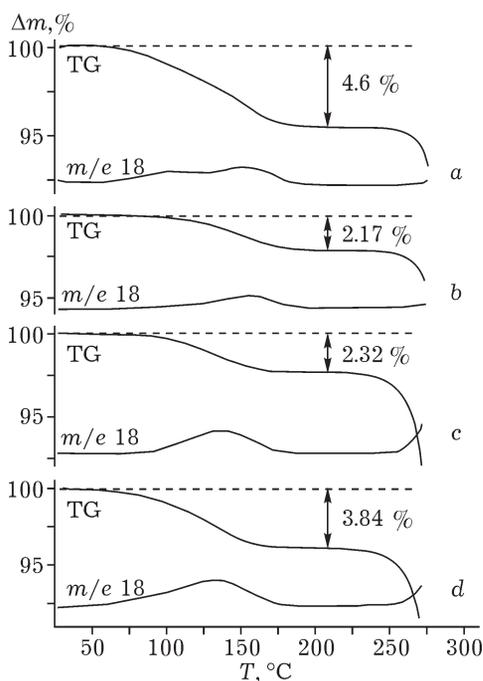


Fig. 5. Loss of water mass depending on temperature in the initial sample (a), after its drying at 100 °C (b) and after annealing at 200 °C followed by exposure for 1 (c) and 3 days (d).

of water and CO₂ as a result of the decomposition of citrate ions. Crystal water is evolved from the samples within a broad temperature range (50–180 °C). Decomposition of citrate ions in the oxidative atmosphere starts at about 220 °C. Mass loss at the first stage, connected with the removal of water (endo effect at 135 °C), is 4.6 % (Fig. 5, a), which corresponds to the initial composition $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot 1.15\text{H}_2\text{O}$. Excess water content in the compound above 1.0 (one H₂O molecule in the formula of the compound corresponds to 4.0 mass % H₂O) in our opinion is due to the presence of adsorbed water. High mobility of water in the compound must be stressed. In the case of drying at 100 °C for 60 min and subsequent recording of thermogram, mass change connected with water removal is 2.17 % (see Fig. 5, b). Water is completely removed during sample exposure at 200 °C for 4 h; however, when kept in the air in closed polyethylene pack, mass change during thermogram recording 24 h later is 2.32 % (see Fig. 5, c), while after 8 days it is 3.84 % (see Fig. 5, d), which corresponds to the composition $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot 0.97\text{H}_2\text{O}$. It must be noted that after exposure of the crucible with annealed sample for 20 h in the air the compound contains 4.0 mass % water.

In order to optimise the synthesis of the target product and decrease energy consumption during its crystallisation from solution, determination of the mass ratio of the aqueous solution of potassium hydroxide to bismuth citrate is of interest. Investigations provide evidence that the treatment of 100 g (0.251 M) of bismuth citrate with 90 mL of KOH solution with the concentration 2.8 mol/L, including mixing for 30 min at the process temperature of 22 °C and subsequent drying of the paste-like product at (70±10) °C leads to the formation of $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot \text{H}_2\text{O}$. In this case, the molar ratio of bismuth to potassium, as well as the mass ratio of the solution of potassium hydroxide to bismuth citrate in the system, are equal to 1.0. For the mass ratio of potassium hydroxide to bismuth citrate in the system less than 0.5, the interaction proceeds not completely, and the product contains unreacted bismuth citrate as admixture, while for the ratio larger than 2.0 the large volume of resulting solution

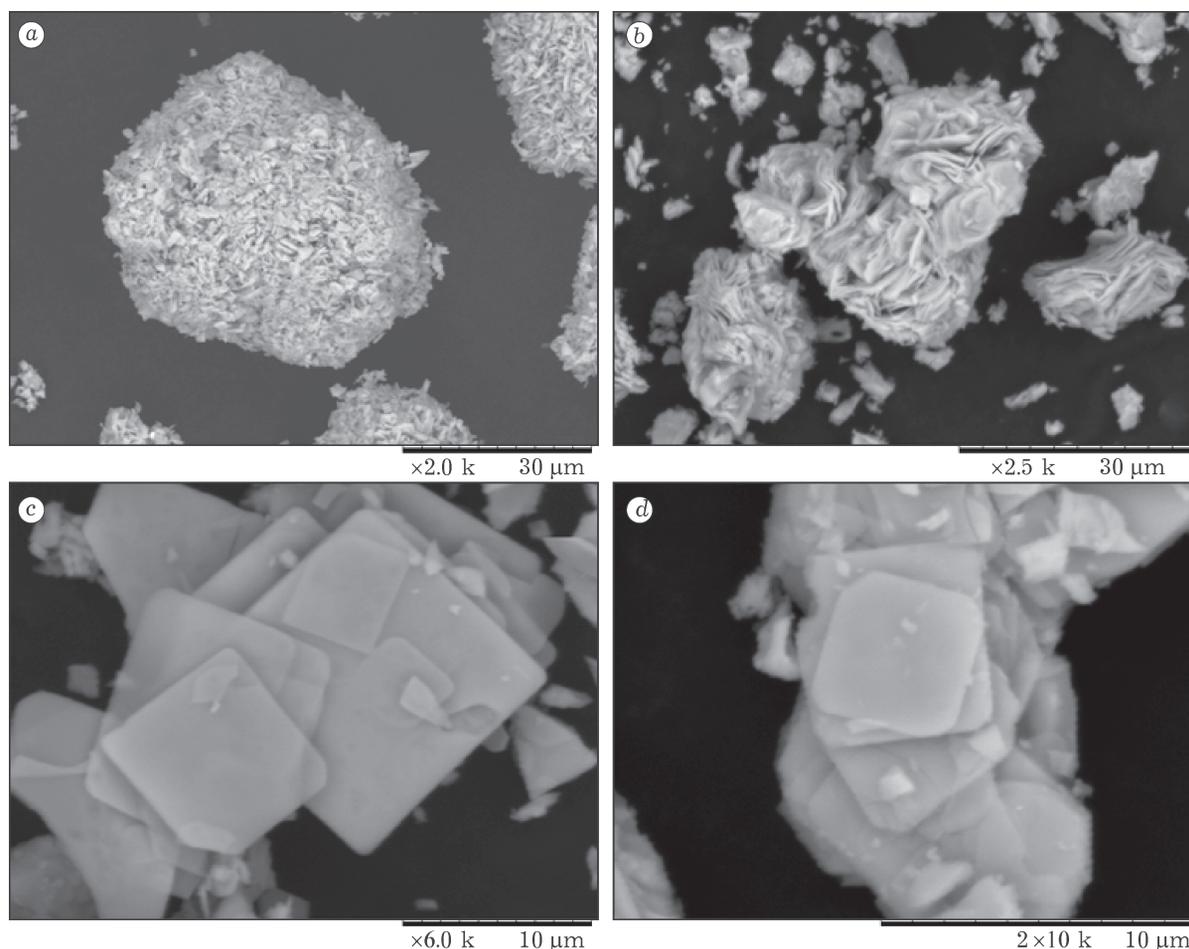


Fig. 6. Micrographs of the samples of initial bismuth citrate (a) and bismuth-potassium citrate monohydrate (b-d) obtained as a result of the treatment of bismuth citrate with the solution of potassium hydroxide (b), its crystallization from bismuth-containing solution (c) and after annealing the crystallization product at 200 °C for 3 h (d).

requires increased energy consumption for its treatment by means of crystallization.

The results of electron microscopic studies (Fig. 6, a) provide evidence that the initial bismuth citrate is composed of the aggregates 10–50 μm in size, in turn, the aggregates are composed of fine crystals about 1–3 μm in size. The samples of bismuth-potassium citrate monohydrate obtained through the treatment of bismuth citrate with the aqueous solution of potassium hydroxide at their molar and mass ratio equal to 1.0 are aggregates 3–30 μm in size, comprised by plate-like crystals (see Fig. 6, b), while the specific surface of the product is 1.42 m²/g. In the case of crystallization from the solution with bismuth concentration 55 g/L, as a result of evaporation, bismuth-potassium citrate is composed of plate-like square crystals with the dimensions from 5 × 5 to 15 × 15 μm,

about 0.1–0.2 mm thick (see Fig. 6, c). The specific surface of the product is 0.84 m²/g. It should be noted that in the case of water removal from bismuth-potassium citrate by annealing at 200 °C for 3 h, followed by cooling and exposure in the air for 10 days, the morphology of the product is conserved (see Fig. 6, d).

CONCLUSION

Investigations provide evidence that the treatment of bismuth citrate with the solution of potassium hydroxide can result in obtaining the solutions with bismuth concentration 60 g/L. It is shown that bismuth potassium citrate used in medicine can be obtained in the form of monohydrate having the composition $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot \text{H}_2\text{O}$ either as a result of evapora-

tion of bismuth-potassium citrate containing solutions or by treating bismuth (III) citrate with the aqueous solution of potassium hydroxide at their molar and mass ratio equal to 1.0. In the latter case, the degree of bismuth extraction into the product is not less than 99.9 %, so only drying of the resulting paste-like product at (70 ± 10) °C is necessary.

REFERENCES

- 1 Mashkovskiy M. D., *Lekarstvennyye Sredstva*, RIA "Novaya Volna", Moscow, 2008.
- 2 Briand G. G., Burford N., *Chem. Rev.*, 99, 9 (1999) 2601.
- 3 Yukhin Yu. M., Mikhailov Yu. I., *Khimiya Vismutovykh Soyedineniy i Materilov*, Izd-vo SO RAN, Novosibirsk, 2001.
- 4 Herrmann W. A., Herdweck E., Pajdla L., *Inorg. Chem.*, 30, 12 (1991) 2579.
- 5 Palkina K. K., Kuchshinova T. B., Skorikov V. M., *Zh. Neorg. Khim.*, 50, 9 (2005) 1461.
- 6 Antsyshkina A. S., Sadikov G. G., Kuvshinova T. B., Skorikov V. M., Sergienko V. S., *Zh. Neorg. Khim.*, 51, 3 (2006) 423.
- 7 Yukhin Yu. M., Afonina L. I., Daminova T. V., Danilova L. E., *Zh. Prikl. Khim.*, 73, 1 (2000) 11.
- 8 Eshvort M. R. F., *Titrimetric Organic Analysis, part II: Indirect Methods*, Intersci. Publishers, New York, 1965.
- 9 Bellamy L., *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley & Sons, New York, 1958.
- 10 Vanhoyland G., Pagnaer J., D'Haen J., Mullens S., Mullens J., *J. Solid State Chem.*, 178 (2005) 166.
- 11 Deacon G. B., Phillips R. J., *Coord. Chem. Rev.*, 33, 3 (1980) 227.
- 12 Barrie P. J., Djuran M. I., Mazid M. A., McPartlin M., Sadler P. J., Scowen I. J. and Sun H., *J. Chem. Soc., Dalton Trans.*, 12 (1996) 2417.
- 13 Asato E., Katsura K., Mikuriya M., Fujii T., Reedijk J., *Inorg. Chem.*, 34, 9 (1995) 2447.