Thermochimica Acta 502 (2010) 90–93

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Short communication

Synthesis and thermal decomposition of $[Bi_6O_4(OH)_4](NH_2SO_3)_6$

A. Zahariev[a,*], V. Parvanova[b], N. Kaloyanov[c]

[a] *Department of Chemistry, Technical University, 8 St. Kliment Ohridski Blvd., 1000 Sofia, Bulgaria*
[b] *Department of General and Inorganic Chemistry, University of Chemical Technology and Metallurgy, 8 St. Kliment Ohridski Blvd., 1756 Sofia, Bulgaria*
[c] *Department of Organic Chemistry, University of Chemical Technology and Metallurgy, 8 St. Kliment Ohridski Blvd., 1756 Sofia, Bulgaria*

ARTICLE INFO

Article history:
Received 17 November 2009
Received in revised form 26 January 2010
Accepted 31 January 2010
Available online 10 February 2010

Keywords:
Bi(III) complexes
Thermal decomposition
X-ray diffraction
DTA–TG

ABSTRACT

The interaction of Bi(III) with aqueous solution of sulfamic acid is investigated, and a new compound with the following composition $[Bi_6O_4(OH)_4](NH_2SO_3)_6$ is derived. The substance obtained is characterized by various methods: elemental analysis, DTA, TG, FTIR and X-ray diffraction. Based on the experimental results, a mechanism of thermal decomposition of the newly synthesized compound is proposed.

1. Introduction

The synthesis and characterization of Bi(III) compounds with various inorganic and organic anionic species is a subject of thorough investigations [1]. There are a small number of water soluble inorganic salts of Bi(III) derived by interaction of Bi(III) with strong-acid anions (e.g. nitrate, sulfate, and perchlorate). However, in a weak acidic and alkaline environment they hydrolyze to a series of poorly soluble compounds because of the formation of polycations of composition $[Bi_6O_x(OH)_{8-x}]^{(10-x)+}$ depending on solution's pH [2]. Within pH 1.0–1.2, a species having composition $[Bi_6O_4(OH)_4]^{6+}$ is generated [2–5]. Therefore, determining the composition and investigating the properties of Bi(III) salts in aqueous solutions are oftentimes accompanied by serious difficulties.

Despite the peculiarities mentioned about complicated Bi(III) pH dependent behaviour, a series of its complexes with various ligands have been synthesized and characterized. Most important of them are the complexes with hydroxidocarboxylic and aminocarboxylic acids. In the recent years, the interest to the synthesis of Bi(III) compounds containing various acidic anions raised significantly due to the implementation of a variety of these compounds in the production of antibacterial medicines [1]. A lot of these compounds contain variable number of water molecules, and many double hydrates containing Na^+, K^+ and NH_4^+ have been synthesized as well. The tartaric- [6–8] and citric acid [9,10] complexes have been most widely investigated, and for many of them the crystalline structure has been ascertained. There is also a plenty of complexes with anions of gallic, malonic, lactic, nitrilotriacetic and ethylenediaminetetraacetic acids depicted [11–13]. Recently, data about the synthesis of Bi(III)-stearate and Bi(III)-oxidohydroxidolaurate have been reported [14,15].

However, data about the interaction between Bi(III) and sulfamic acid are not found in the literature. Therefore, it is of great interest to investigate this interaction and to characterize the product obtained in view of its potential implementation as a biologically active substance.

2. Experimental

The interaction of Bi(III) with sulfamic acid was performed as follows: 40 g $Bi(NO_3)_3{\cdot}5H_2O$ (Merck, p.a.) were added to 170 cm^3 12% (pH 1.0–1.2) aqueous solution of HNH_2SO_3 (Fluka puriss. p.a.) The experimental conditions included 96 h of stirring at room temperature because of the substantial hydrolysis of $NH_2SO_3^-$ at higher temperatures [16]. The white precipitate obtained was firstly washed with mother water, then with double distilled water up to pH 7.0, and finally dried in a desiccator over P_4O_{10}. The product's composition was determined by elemental analysis on VarioELV5.18.018 (Elementar Analysensysteme GmbH, Hannau, Germany) performing in CHNS mode. The data presented, indicated by the symbols of the elements, are within ±0.40% of the theoretical values:

Calcd. %: N – 4.28; S – 9.78; H – 0.81;
Found %: N – 4.30; S – 9.44; H – 1.03.

---

[*] Corresponding author.
E-mail address: alexs_zahariev@yahoo.com (A. Zahariev).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.01.026

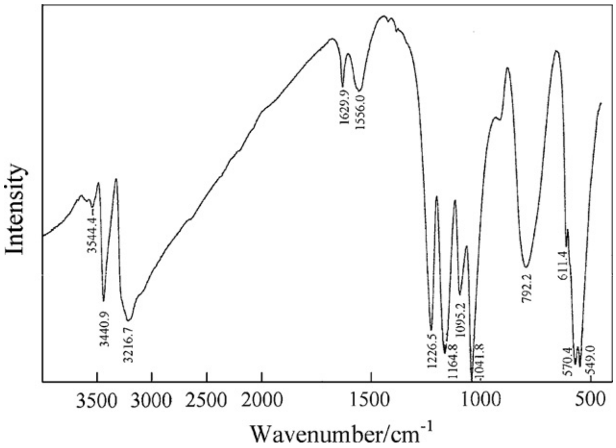

Fig. 1. FTIR spectrum of $[Bi_6O_4(OH)_4](NH_2SO_3)_6$.

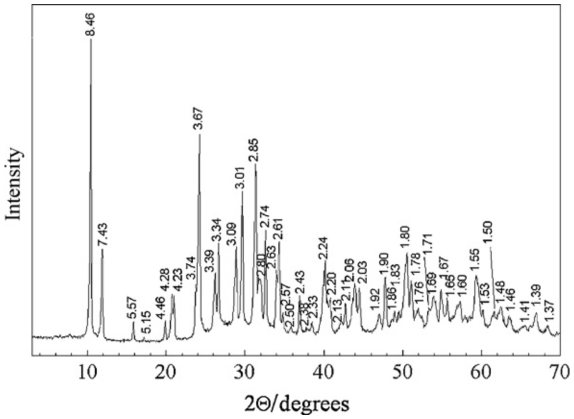

Fig. 2. X-ray diffraction pattern of $[Bi_6O_4(OH)_4](NH_2SO_3)_6$.

Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer in the range of 4400–450 cm^{-1}, resolution 4 cm^{-1} in KBr pellets.

DTA–TG measurements were performed on Derivatograph Q-1500-D (MOM, Hungary), within 20–1000 °C and 10 °C min^{-1} rate in air, using Al_2O_3 as an inert substance. The sample mass used was 500 mg.

The final product and intermediate phases after DTA–TG analysis (at 240, 320, 440 and 620 °C) were characterized by X-ray diffraction (XRD) on automated Siemens D 500 apparatus with 40 kV Cu Kα radiation within $2\theta = 3–70°$.

3. Results and discussion

In Fig. 1, the FTIR spectrum of $[Bi_6O_4(OH)_4](NH_2SO_3)_6$ is presented. It is obvious that the most characteristic bands of the sulfamic acid [17] could be found within the spectrum of the compound synthesized. Its absorption bands, referred to the most likely vibrations of different functional groups, are given in Table 1.

Within the spectrum under consideration, a broad medium band at 792 cm^{-1} appears as well, assigned most probably to bending vibration of the bridging oxygen atom in Bi–O–Bi species [18].

The X-ray diffraction pattern of the compound under investigation is shown in Fig. 2. It is clearly seen from the figure that a high-level crystalline phase appears.

In Fig. 3 the results from DTA–TG analyses of new compound within the range 20–1000 °C are presented. Both FTIR and XRD analyses are also used in the investigation of the DTA–TG intermediate phases formed at different temperatures. The results of these supporting investigations are summarized in Figs. 4 and 5.

Table 1
FTIR spectral data and band assignments of $[Bi_6O_4(OH)_4](NH_2SO_3)_6$.

FTIR, cm^{-1}	Assignment
3441 s	ν_{as} NH_2
3212 sh	ν_s OH + ν_s NH_2
1629 w	δ S–OH (scissoring)
1553 w br	δ NH_2
1226 s	δ OH
1164 s	ω NH_2 + ν S═O
1095 m	
1041 vs	r NH_2 + ν S–O
792 m br	Bi–O–Bi
610 m	δ SO_2 (scissoring)
570 s	
546 vs	ω SO_2 (wagging)

Considering Fig. 3, a clearly outlined exothermic peak at 230 °C appears, and at the same time no mass loss is observed at this temperature. In Fig. 4a, FTIR spectrum of the phase at 240 °C reveals a decrease in the intensity of vibrations at 1553 cm^{-1} and 792 cm^{-1}, compared to those of the initial substance (Fig. 1). Furthermore, a new absorption band at 1402 cm^{-1} could be discerned. In Fig. 1, four absorption bands within 1050–1170 cm^{-1} appear due to the stretching vibrations of the S═O and S–O bonds in SO_3. The bands' description gives reason to assume that $[Bi_6O_4(OH)_4](NH_2SO_3)_6$ is generally well crystallized. Taking into consideration the data from DTA–TG and FTIR, one can conclude that with the increasing the temperature up to 230 °C, a polymorphic re-crystallization most probably proceeds, and as a result, a thermodynamically more stable phase is formed. On the other hand, partial transformation

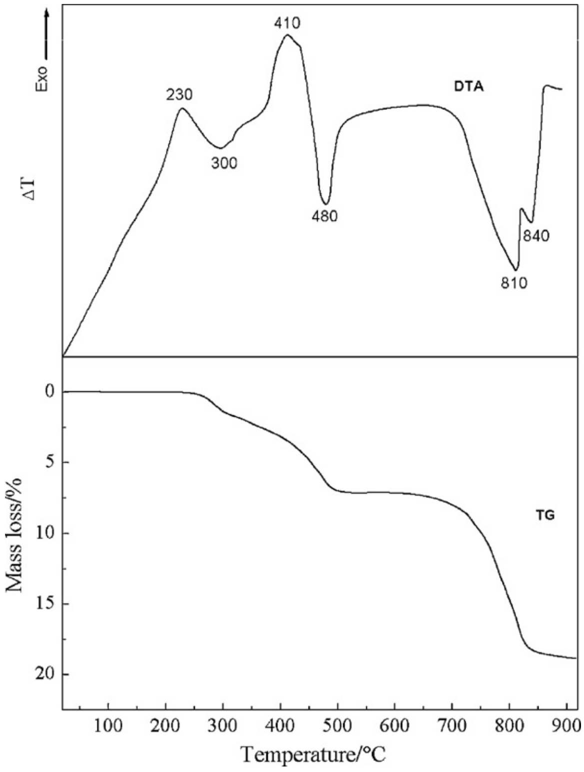

Fig. 3. DTA–TG curves of $[Bi_6O_4(OH)_4](NH_2SO_3)_6$.

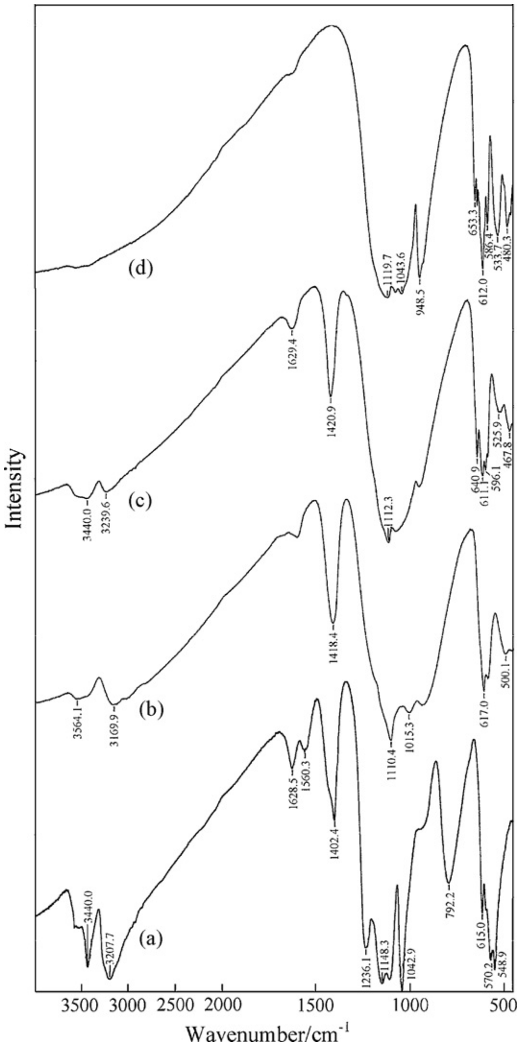

Fig. 4. FTIR spectra of phases derived at different temperatures as follows: (a) 240 °C; (b) 320 °C; (c) 440 °C; (d) 620 °C.

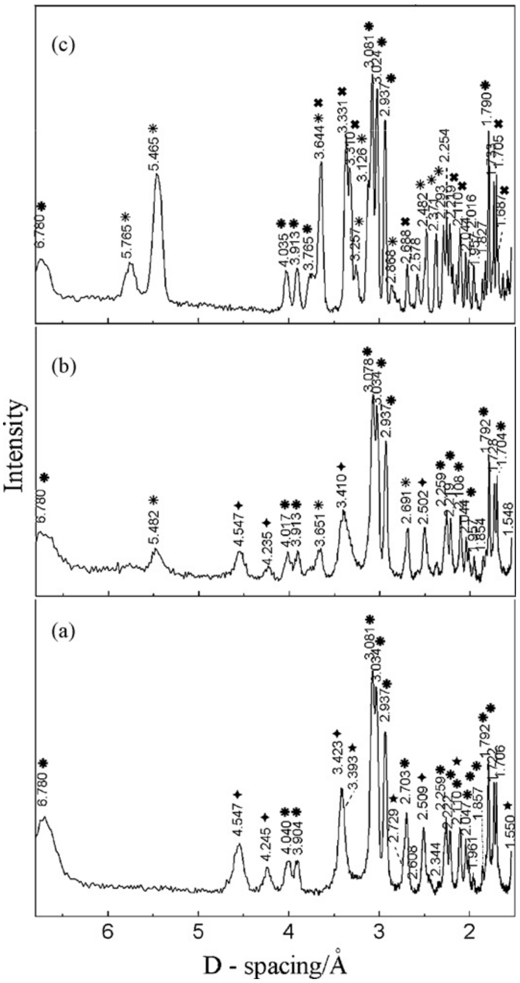

Fig. 5. XRD patterns of phases derived at different temperatures: (a) 320 °C; (b) 440 °C; (c) 620 °C. The separate phases are denoted as follows: (✱) $Bi_2O_2SO_4$; (✦) $Bi_4\{NH(SO_3)_2\}_4(OH)_4$; (★) $[Bi_6O_4(OH)_4](NH_2SO_3)_6$; (✳) $Bi_2O(SO_4)_2$; (✖) $Bi_2O(OH)_2SO_4$.

of SO_3 into SO_4 may take place. Both changes could explain the widening, shift and partial merging some bands within the range mentioned.

Within the temperature range of 230–410 °C (Fig. 3) in the DTA curve, an endothermic peak at 300 °C is obvious, and mass loss Δm 2.00% (calcd. 2.30%) is registered following the TG curve. In Fig. 4b, the FTIR spectrum of the phase formed at 320 °C is presented. The figure reveals that the bands at 1553 cm^{-1} and 792 cm^{-1} entirely disappear, while the new band at 1402 cm^{-1} becomes more intensive and shifts towards 1418 cm^{-1}. This band could most likely be explained by bending vibrations of NH-group [19]. Likewise, from XRD (Fig. 5a) two new phases appear at 320 °C, one of which is the well known $Bi_2O_2SO_4$ [20]. The second phase most probably corresponds to the composition containing imidosulfonate species $Bi_4\{NH(SO_3)_2\}_4(OH)_4$, which is not described in the literature. One can judge about the existence of this presumable composition by the elemental analysis performed on the solid remainder after heating the initial compound up to 320 °C (calcd. %: N – 2.47; S – 10.16; Found %: N – 2.28; S – 10.02).

At 410 °C (Fig. 3), a new exothermic peak appears coupled with a slight mass increase which is probably due to oxygen incorporation from the air. After a short delay of the decomposition rate (Δm 2.00%; calcd. 2.30%), a large endothermic peak at 480 °C corresponding to a mass loss Δm 3.00% (calcd. 2.96%) is recorded. In Fig. 5b, the formation of another known phase $Bi_2O(SO_4)_2$ is observed at 440 °C [21].

At 620 °C, the absorption band at 1418 cm^{-1} (Fig. 4d) completely disappears. Along with the elemental analysis (Found %: N – 0.08) of the remainder at this temperature, this reveals the entire separation of nitrogen. In Fig. 5c, the simultaneous presence of three oxido- and oxidohydroxidosulfates of Bi(III), i.e. $Bi_2O_2SO_4$, $Bi_2O(SO_4)_2$ [21] and $Bi_2O(OH)_2SO_4$ [22] is clearly seen.

Two consequent endothermic peaks appear in Fig. 3 at 810 and 840 °C, respectively, coupled with substantially stronger sample's mass decrease (Δm 11.40%), which is probably caused by the evolution of large amount of SO_3.

When comparing the thermal stability of $[Bi_6O_4(OH)_4](NH_2SO_3)_6$ with other similar compounds: $[Bi_6O_4(OH)_4](C_{11}H_{23}COO)_6$ [14], $[Bi_6O_4(OH)_4](C_{17}H_{35}COO)_6$ [15] and $[Bi_6O_6(OH)_3](NO_3)_5{\cdot}1.5H_2O$ [4] it is clearly visible that the initial decomposition temperatures lie within a short range (180–250 °C). However, while the above mentioned complexes decompose completely to Bi_2O_3 within the range 500–600 °C, for $[Bi_6O_4(OH)_4](NH_2SO_3)_6$ this temperature is significantly higher (above 840 °C).

Based on the results from DTA–TG, FTIR, XRD and elemental analyses, the following most probable mechanism of the thermal decomposition of $[Bi_6O_4(OH)_4](NH_2SO_3)_6$ within 20–620 °C could be proposed:

$$3[Bi_6O_4(OH)_4](NH_2SO_3)_6 \xrightarrow{20-320\,^{\circ}C} 4Bi_2O_2SO_4 + 8NH_3 + [Bi_6O_4(OH)_4](NH_2SO_3)_6 + Bi_4\{NH(SO_3)_2\}_4(OH)_4$$

$$[Bi_6O_4(OH)_4](NH_2SO_3)_6 + Bi_4\{NH(SO_3)_2\}_4(OH)_4 + 4Bi_2O_2SO_4 + 1.5O_2 \xrightarrow{320-440\,^{\circ}C} 4NH_3 + N_2 + 2H_2O + 4Bi_2O_2SO_4 + 3Bi_2O(SO_4)_2 + Bi_4\{NH(SO_3)_2\}4(OH)_4$$

$$4Bi_2O_2SO_4 + 3Bi_2O(SO_4)_2 + Bi_4\{NH(SO_3)_2\}_4(OH)_4 \xrightarrow{440-620\,^{\circ}C} 2NH_3 + N_2 + SO_2 + SO + Bi_2O_2SO_4 + 7Bi_2O(SO_4)_2 + Bi_2O(OH)_2SO_4$$

4. Conclusion

During investigation of the interaction between Bi(III) and sulfamic acid in aqueous medium, at ambient temperature and pH 1.0–1.2, a compound with composition $[Bi_6O_4(OH)_4](NH_2SO_3)_6$ is prepared. This compound is characterized by various analytical methods: elemental analysis, DTA–TG, FTIR and XRD. The results from these analyses reveal that the substance obtained is well crystallized. Furthermore, the most probable mechanism of thermal decomposition of $[Bi_6O_4(OH)_4](NH_2SO_3)_6$ within 20–620 °C is described and it is in accordance with the analyses carried out.

References

[1] G.G. Briand, N. Burford, Chem. Rev. 99 (1999) 2601–2657.
[2] N. Henry, O. Mentre, F. Abraham, E.J. McLean, P. Roussel, J. Solid State Chem. 179 (2006) 3087–3094.
[3] B. Sundvall, Acta Chem. Scand. A 33 (1979) 219–224.
[4] A.N. Christensen, M.A. Chevallier, J. Skibsted, B.B. Iversen, J. Chem. Soc. Dalton Trans. 3 (2000) 265–270.
[5] A.N. Christensen, T.R. Jensen, N.V.Y. Scarlett, I.C. Madsen, J.C. Hanson, A. Altomare, J. Chem. Soc. Dalton Trans. 16 (2003) 3278–3282.
[6] M. Girard, J. Lecomte, J. Phys. Radium 17 (1956) 9–15.
[7] W.A. Hermann, E. Herdtweck, W. Scherer, P. Kiprof, L. Pajdla, Chem. Ber. 126 (1993) 51–56.
[8] D.S. Sagatys, E.J. O'Reilly, S. Patel, R.C. Bott, D.E. Lynch, G.S. Smith, H.L. Kennard, Aust. J. Chem. 45 (1992) 1027–1034.
[9] E. Asato, W.L. Driessen, R.A.G. De Graaff, F.B. Hulsbergen, J. Reedijk, Inorg. Chem. 30 (1991) 4210–4218.
[10] E. Asato, C.M. Hol, F.B. Hulsbergen, N.T.M. Klooster, J. Reedijk, Inorg. Chim. Acta 214 (1993) 159–167.
[11] A. Radecki, M. Wesolowski, Thermochim. Acta 17 (1976) 217–229.
[12] M. Devillers, F. De Smet, O. Tirions, Thermochim. Acta 260 (1995) 165–185.
[13] P. Kiprof, W. Scherer, L. Pajdla, E. Herdtweck, W.A. Herrmann, Chem. Ber. 125 (1992) 43–46.
[14] A.V. Minina, Y.M. Yukhin, B.B. Bokhonov, I.A. Vorsina, Y.I. Mikhailov, L.E. Danilova, Chem. Sust. Develop. 11 (2003) 371–378.
[15] Y.M. Yukhin, K.I. Mikhailov, B.B. Bokhonov, I.A. Vorsina, Chem. Sust. Develop. 12 (2004) 403–408.
[16] G.A. Benson, W.J. Spillane, Chem. Rev. 80 (1980) 151–186.
[17] D. Philip, A. Eapen, G. Aruldhas, J. Solid State Chem. 116 (1995) 217–223.
[18] K. Inumaru, A. Ono, H. Kubo, M. Misono, J. Chem. Soc. Faraday Trans. 94 (1998) 1765–1770.
[19] M. Tatsuo, J. Mol. Spectrosc. 4 (1960) 155–167.
[20] JCPDS 41-0688.
[21] JCPDS 78-2087.
[22] JCPDS 76-1102.