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Short communication

Synthesis and thermal decomposition of [Bi₆O₆(OH)₂](NH₂C₆H₄SO₃)₄

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ABSTRACT

An investigation of the interaction of Bi(III) with an aqueous solution of sulfanilic acid at a higher temperature is performed. As a result, a new composition $[Bi_6O_6(OH)_2](NH_2C_6H_4SO_3)_4$ is precipitated. This Bi(III) complex is characterized by various methods: elemental analysis, DTA, TG–MS, DSC, FTIR, and powder X-ray diffraction. Based on the experimental results, X-ray diffraction indexation as well as thermal decomposition products of the compound are suggested.

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1. Introduction

Bi(III) complexes with different ligands have found an increasing implementation in medicine as a main ingredient of modern antimicrobial and antitumour agents [1–3]. In most cases, however, the synthesis of bismuth compounds with various inorganic and organic anionic species in aqueous environment is accompanied by significant hydrolysis of Bi(III) [3]. A series of insoluble compounds containing polycations with a general formula $[Bi_6O_x(OH)_{8-x}]^{(10-x)+}$ have been isolated, as *x* varies with pH of the solution [4,5]. Within pH 2.7–3.5 a species having composition $[Bi_6O_6(OH)_2]^{4+}$ has been formulated [6,7].

Recently, a number of novel Bi(III) complexes with organic and inorganic ligands have been demonstrated. The tartaric- [8–10], citric- [11,12] as well as oxalic acid [13–15] complexes have been a subject of a thorough investigation. Other complexes containing anions of gallic, malonic, lactic, nitrilotriacetic and sulfamic acids have been reported [16–18]. Synthesis of various Bi(III)oxidohydroxidocarboxylates has been performed as well [19].

Currently, some of the newest routes of synthesizing Bi(III) compounds appear to be the development of coordination oxoclusters [20], as well as the development of different mixed oxide systems [21,22].

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Nothing is found in the literature regarding the interaction between Bi(III) and sulfanilic acid. On that account, investigating this interaction and its resulting product could complement the existing developments within the comparatively less explored Bi(III) chemistry.

2. Experimental

The interaction of Bi(III) with sulfanilic acid was performed as follows: 0.4g Bi_2O_3 (Merck, 99.5%) were added to 1.0 dm^3 1% aqueous solution of $\text{HNH}_2C_6\text{H}_4\text{SO}_3$ (pH 2.7) (Merck, >98%). The experimental conditions included 96 h of stirring at temperature 70 °C because of the low solubility of the acid. The white-yellowish precipitate obtained was rinsed with hot double distilled water until the outgoing water reached pH 7.0 to remove any acid residuals. Afterwards, the product was dried in a desiccator over silica gel.

The product's composition was determined by elemental analysis on VarioELV5.18.018 (Elementar Analysensysteme GmbH, Hannau, Germany) performing in CHNS mode.

Infrared spectra were recorded on Varian 660-IR FTIR Spectrometer within 4000–450 cm⁻¹, in KBr pellets, and in terms of the water vibrations–in Nujol suspension rather than in KBr.

Powder X-ray diffraction (XRD) patterns were collected within the range of $3-77^{\circ} 2\theta$ with a constant step of $0.02^{\circ} 2\theta$ on Bruker D8 Advance diffractometer with Cu K_{\alpha} radiation and LynxEye detector.

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Fig. 1. FTIR spectrum of [Bi₆O₆(OH)₂](NH₂C₆H₄SO₃)₄.

The data were evaluated by the Diffracplus EVA and Topas 4.2. packages.

DTA-TG measurements were performed on LABSYSTM evo (SETARAM) within 20–1000 °C and 10 °C min⁻¹ rate in Ar atmosphere by flow rate 20 cm³ min⁻¹. A thermostated balance that uses the technique of a beam articulated around a torsion band is in operation. The sample mass used was 25.0 mg; the weighing precision is $\pm 0.01\%$. Empty alumina crucible was used as a reference sample. Gas analyzer OmniStarTM by Pfeiffer Vacuum was used to determine the qualitative composition of gases released.

Also, a DSC analysis was performed on a scanning calorimeter Stanton Redcroft (England) within 0–650 °C and a heating rate of $5 \circ C \min^{-1}$. Sample mass used was 6.0 mg taking Pt crucible and the latter is used empty as a reference. Inert (Ar) atmosphere was ensured during the DSC measurements.

The endothermic peaks visible within DTA and DSC curves and the corresponding mass loss (Δm) of the samples were analyzed. On this basis, the temperature ranges were defined within which an additional isothermal heating of the compound synthesized was carried out. Samples were heated in consecutive 10 °C steps in the 360–520 °C range until reaching a constant sample mass, followed by a calculation of the mass decrease (Δm , %) of each sample. Two temperatures (410 °C and 500 °C) were selected. They correspond to the samples whose Δm coincides with Δm from TG curve. The mass change according to TG curve was measured up to its track change. The mass (m) of each initial sample was 1.0 g and was heated for 2 h. After heating, the samples were cooled out (25 °C) and kept in a dessicator over silica gel. Their composition was identified by FTIR and powder XRD analyses.

3. Results and discussion

The data from the elemental analysis of the complex synthesized indicated by the symbols of the elements are presented below and are within $\pm 0.40\%$ of the theoretical values.

Calcd.%: N - 2.70; C - 13.89; S - 6.18; H - 1.25

Found% : N – 2.68; C – 13.56; S – 6.00; H – 0.92.

In Fig. 1 FTIR spectrum of the synthesized compound is presented. From this figure the bands of SO_3^- group, characteristic vibrations of 4-disubstituted aromatic ring as well as those of the amino group [23,24], are identified. Within the range 3600–3100 cm⁻¹, an overlap of the stretching vibrations of OH with those of the amino group is visible. Also, the bending vibrations of both functions could be

Table 1

FTIR spectral data and band assignments of [Bi₆O₆(OH)₂](NH₂C₆H₄SO₃)₄.

FTIR (cm ⁻¹)	Assignment
3535	vOH (shoulder)
3448	$v_{as}NH_2$
3353	$\nu_{s}NH_{2}$
3050	vC–H (from Ar)
1627	$\delta_{scis}NH_2$
1599–1430	$\nu C = C (from Ar)$
1300	vN-C
1180	$v_{as}SO_2$
1124	δBi–OH
1026	$\nu_{s}SO_{2}$
829	γ_{C-H} p-disubstituted Ar (out of plane bending)
698	$\delta_{W}N-H$
565	vBi-O
469	δBi–O

recognized at 1124 cm⁻¹ (δ Bi–OH) [30], at 1627 cm⁻¹ ($\delta_{scis}NH_2$) as well as at 698 cm⁻¹ (δ_w N–H). At 565 cm⁻¹ and 469 cm⁻¹ two bands appear, corresponding to ν Bi–O and δ Bi–O, respectively [25]. In Table 1 the values of vibrations and their corresponding functional groups are presented.

Based on the data from the elemental analysis and FTIR spectrum, the following stoichiometric composition of the Bi(III)-complex could be ascertained: $[Bi_6O_6(OH)_2](NH_2C_6H_4SO_3)_4$. This composition represents also the ratio 3:2 between Bi-sulfanilic acid anion.

In Fig. 2 the XRD pattern of the newly prepared complex is presented. Within this figure no one of the known Bi(III)-containing phases is found. Therefore, the diffraction pattern is indexed within the tetragonal I4 space group with unit cell parameters a = 26.5122 Å and c = 5.7613 Å. X-ray diffraction data of the initial compound after indexation are presented in Table 2.

The thermal decomposition of $[Bi_6O_6(OH)_2](NH_2C_6H_4SO_3)_4$ is studied by DTA and TG-analyses (Fig. 3) coupled with massspectrometry, differential scanning calorimetry (Fig. 4), X-ray diffraction (Fig. 5), and FTIR spectrometry (Fig. 6).

A large endothermic effect is observed in DTA-curve (Fig. 3) in the temperature range of $360-520 \circ C$ with $T_{max} = 415 \circ C$, while in DSC-curve (Fig. 4) two endothermic effects appear within the same range.

The first endothermic effect in DSC is split into two peaks with T_{max} = 411.6 °C and T_{max} = 419.7 °C, respectively. The second one is considerably weaker and is observed at T_{max} = 452.9 °C. The difference found in the tracks of DTA and DSC curves could be explained by the higher resolution of the DSC method. From 360 °C to 520 °C



Fig. 2. XRD pattern of [Bi₆O₆(OH)₂](NH₂C₆H₄SO₃)₄.

Table 2	
X-ray diffraction data from indexing the $[Bi_6O_6(OH)_2](NH_2C_6H_4SO_3)_4$.	

2 heta (°)	d_{\exp} (Å)	I (%)	hkl	$d_{\text{calc}}\left(\text{\AA}\right)$
4.72	18.7456	100	110	18.7469
6.66	13.2596	16	020	13.2561
10.58	8.3278	1	130,310	8.3888
14.19	6.2366	2	330	6.2490
14.94	5.9203	2	420,240	5.9283
17.09	5.1746	1	121,211	5.1819
19.61	4.5291	2	321,231	4.5351
20.75	4.2876	1	141,411	4.2909
22.83	3.8926	2	051,341,431	3.9015
23.77	3.7359	1	251,521	3.7428
26.51	3.3564	9	541,451	3.3623
27.37	3.2535	3	631,361	3.2591
28.99	3.0747	1	271,721	3.0783
30.55	2.9224	8	561,651	2.9246
31.33	2.8540	4	181,811,471,741	2.8560
32.78	2.7269	1	132,312	2.7243
33.81	2.6450	2	042	2.6419
34.51	2.5950	2	1020,2100	2.5997
37.49	2.3969	1	1101,1011	2.3986
39.38	2.2821	1	712,552,172	2.2843
44.17	2.0569	2	1211,981,891,1121	2.0566
47.08	1.9275	1	2102,1022	1.9299
48.80	1.8641	2	1091,9101	1.8646
51.89	1.7593	1	163,613	1.7574
54.84	1.6728	1	653,563	1.6715
56.56	1.6290	1	1262,6122	1.6295
58.92	1.5665	1	1631,3161,12111,11121	1.5672

the TG-curve changes twice its character (Fig. 3). From experimental data obtained by DTA, TG, and DSC, it can be concluded that in the temperature range under consideration the thermal decomposition of $[Bi_6O_6(OH)_2](NH_2C_6H_4SO_3)_4$ occurs in two stages. For confirmation of this statement, an isothermal heating (410 °C and 500 °C) of the initial compound's samples is performed.

Mass loss $\Delta m = 16.8\%$ calculated from thermogravimetric data within 360–430 °C corresponds to the first endothermic peak (Fig. 3). During the process related to this effect, a simultaneous release of NH₃, NO, CO, and CO₂ is registered as a result of aromatic ring decomposition. The qualitative composition of these gases is established after mass-spectrometric measurements. Furthermore, for this first endothermic effect, enthalpy change $\Delta H^0 = 290.5 \pm 1.0$ kJ mol⁻¹ is calculated using the DSC data. A very good coincidence between mass loss ($\Delta m = 17.0\%$) of the sample heated at 410 °C and Δm derived from the TG-curve is observed.



Fig. 3. TG-DTA curves of $[Bi_6O_6(OH)_2](NH_2C_6H_4SO_3)_4$.



Fig. 4. DSC curve of [Bi₆O₆(OH)₂](NH₂C₆H₄SO₃)₄.

The XRD pattern of this sample (Fig. 5a) represents the following composition: α -Bi₂O₃ [26], Bi₁₄O₂₀SO₄ [27], Bi [28] and an amorphous organic-containing phase. The presence of metallic Bi can be explained taking into consideration the strong reductive action of NH₃, NO, and CO, derived after the decomposition. In the FTIR spectrum of the sample heated at 410 °C (Fig. 6a) the characteristic absorption bands of the functional groups of the phases found in XRD are observed. A broad band at 1116 cm⁻¹ is assigned to the stretching vibrations ν SO₂ from SO₄ groups [23,24]. Within 620–480 cm⁻¹, δ SO₂ and ν Bi–O overlap [25,29]. Moreover, in this spectrum the stretching vibration of OH appears at 3431 cm⁻¹, and in the range of 1034–1186 cm⁻¹ δ OH overlaps with ν SO₂ [30]. There are several bands that belong to groups involved in the



Fig. 5. XRD patterns for solid residuals after isothermal heating at two temperatures: (a) $410 \degree C$; (b) $500 \degree C$. The phases are denoted as follows: **X**, $Bi_{28}O_{32}(SO_4)_{10}$; \blacklozenge , $Bi_{14}O_{20}SO_4$; \blacklozenge , Bi; **X**, Bi_2O_3 .



Fig. 6. FTIR spectra of isothermal heating products: (a) 410 °C; (b) 500 °C.

organic-containing amorphous phase, namely at 1706 cm⁻¹ for ν C=O and at 2929 cm⁻¹ for ν_{as} CH₃ and/or ν_{as} CH₂ moieties. The absence of bands for ν C-H (3050 cm⁻¹) and γ C-H (829 cm⁻¹), as well as bands responding to ν C=C (within 1599–1430 cm⁻¹), confirms the decomposition of the aromatic ring. It is worth saying that in the FTIR spectrum considered (Fig. 6a) the characteristic bands of ν_{as} NH₂ and ν_{s} NH₂ are absent. This is an evidence of the complete transformation of the amino group into NH₃ and NO.

of thermal The second stage decomposition of $[Bi_6O_6(OH)_2](NH_2C_6H_4SO_3)_4$ is described by the endothermic effect of DTA and DSC measurements within 430-520 °C. Considering the TG-curve, $\Delta m = 8.8\%$ appears along the entire stage (Fig. 3). This result is caused by the simultaneous release of CO₂ and H₂O during the amorphous phase decomposition that is proven mass-spectrometrically. Therefore, a sample is heated at 500 °C and the resulting mass loss $\Delta m = 8.5\%$ is calculated. The XRD (Fig. 5b) demonstrates a presence of α -Bi₂O₃, Bi₁₄O₂₀SO₄ and $Bi_{28}O_{32}(SO_4)_{10}$ [31], while at the same time a more complete crystallization of α -Bi₂O₃ and Bi₁₄O₂₀SO₄ can be found out. The amorphous phase is obviously absent, and metallic Bi is already transformed (oxidized) into Bi(III). The expected exothermic effect within DTA- and DSC-curves, and also the mass increase in TG-curve (Figs. 3 and 4) due to the oxidation, are not observed. The reason is the simultaneous overlay of opposite effects. After all, the result is a weak endothermic peak within the DSC-curve presenting $\Delta H^0 = 33.0 \pm 0.5 \text{ kJ mol}^{-1}$. The same reason is responsible for the non-registration of exothermic peaks of crystalline phases' formation. FTIR spectrum of the sample heated at 500 °C (Fig. 6b) correlates to the data of XRD derived at the same temperature. Therein, absorption bands generated by $v_{as}SO_2$ appear at 1154 cm⁻¹. Similarly, at 1099 and 1043 cm⁻¹ absorption bands appear for the stretching $v_{s}SO_{2}$ from SO₄. One can find in the range of 620–480 cm⁻¹ the bands of δ SO₂ and ν Bi–O as well. Furthermore, within the spectrum there are no characteristic bands of OH, CH₃ and C=O groups which confirms that the organic-containing phase is decomposed.

In the course of DTA-curve (Fig. 3) there are two more endothermic peaks with $T_{max} = 710 \degree C$ and $T_{max} = 833 \degree C$. It is observable that no mass loss corresponds to these. The first effect could be related to the polymorphic transformation of α -Bi₂O₃ into δ -Bi₂O₃, and the second – to the melting of δ -Bi₂O₃ [32].

Based on the results from DTA, TG, DSC, XRD, FTIR and massspectrometric analyses, the following conclusions can be derived. During the first stage, the thermal decomposition of $[Bi_6O_6(OH)_2](NH_2C_6H_4SO_3)_4$ is released in the temperature range 360–430 °C. At this stage, the decomposition of the aromatic ring proceeds along with simultaneous evolution of NH₃, NO, CO and CO₂ and the following phases are formed: α -Bi₂O₃, Bi₁₄O₂₀SO₄, Bi, and amorphous organic-containing phase.

The second stage lies within 430–520 °C. At this stage CO₂ and H₂O are released, and after the decomposition of amorphous phase, the Bi₂₈O₃₂(SO₄)₁₀ oxosulfate is formed along with the crystalline phases of the first stage.

4. Conclusions

Bi(III) A complex of with composition a [Bi₆O₆(OH)₂](NH₂C₆H₄SO₃)₄ is synthesized on the basis of Bi_2O_3 and $NH_2C_6H_4SO_3H$, and the conditions of synthesis are defined. The composition is confirmed by elemental analysis and FTIR spectroscopy. Using X-ray diffraction, the symmetry (tetragonal; space group I4) and the unit cell parameters are determined. By means of DTA-TG and DSC analyses, the thermal behaviour of the initial complex is studied. Two stages of thermal decomposition are established along with the composition of the gas phases evolved. Thereafter, the phase composition of the solid residuals derived at both heating stages is resolved by FTIR and XRD.

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