



Research Article

ISSN : 0975-7384  
CODEN(USA) : JCPRC5

## Synthesis, characterization and thermal decomposition of bismuth(III) ternary complexes of phthalate

Qing Zang, Guo-Qing Zhong\* and Yan Zhang

School of Material Science and Engineering, Southwest University of Science and Technology, Mianyang, China

### ABSTRACT

Two new complexes of bismuth nitrate with phthalic acid ( $H_2phth$ ) were synthesized by liquid state reaction. The complexes were characterized by chemical and elemental analyses, Fourier transformed infrared spectra, X-ray powder diffraction and thermogravimetry analysis. Their compositions are  $Bi(phth)(NO_3) \cdot 4H_2O$  and  $Bi(phth)(L-cys)_{0.5} \cdot H_2O$  ( $L-H_2cys = L-cystine$ ), respectively. The crystal structure of the complexes belongs to monoclinic system with lattice parameters of  $a = 1.0792$  nm,  $b = 2.2169$  nm,  $c = 1.0306$  nm and  $\beta = 95.68^\circ$  for  $Bi(phth)(NO_3) \cdot 4H_2O$ ; and  $a = 1.4183$  nm,  $b = 2.2633$  nm,  $c = 1.3753$  nm and  $\beta = 96.49^\circ$  for  $Bi(phth)(L-cys)_{0.5} \cdot H_2O$ , respectively. IR spectra indicate that the bismuth(III) ion in the two complexes is six-coordinated by the carboxyl oxygen atoms from the ligands and oxygen atoms from nitrate ion, respectively. The thermal decomposition processes of the complexes under nitrogen include dehydration and pyrolysis of the ligands, and the final residue at about  $480^\circ C$  is bismuthous oxide.

**Key words:** bismuth(III); ternary complex; phthalic acid; synthesis; crystal structure; thermal decomposition

### INTRODUCTION

As we know, the main group elements do not easily form complexes with organic ligands because of the special properties. But the complexes of the main group metal ions, such as bismuth ion, can possess a certain biologic function. The coordination chemistry of bismuth is currently causing particular interest as a result of its myriad applications in medicine and biochemistry catalysis, ferroelectrics, superconductors, and many other oxide based materials [1-5]. The fifth main group metal compounds including inorganic and metal organic complexes have been studied for decades thanks to the interesting medical, physical properties and material functions [6-8]. In contrast to the comprehensive database of other stable elements in the periodic table, bismuth has possibly the least well established data bank, although bismuth has long been used in medicine. The complexes of bismuth have biological functions, such as sterilization, antibacterial activity, anticancer, and so forth [9-14].

Chemical scholars are concentrating much attention on the synthesis and identification of new bismuth complexes that are suitable for these applications [15]. Bismuth compounds have been widely used in the clinic because of their higher effectiveness and lower toxicity in the treatment of a kind of microbial infections, including syphilis, diarrhea, gastritis and colitis [16-18]. The research of bismuth interactions with potential targeting biomolecules, including peptides, proteins and enzymes, will bring about an understanding of the mechanism of action of bismuth-containing complexes and in turn to the further application of bismuth in medicine [19, 20].

We have a great interest in the coordination chemistry of bismuth, and demonstrate that polycarboxylic frameworks are able to accommodate bismuth [21-24]. The inorganic salts of bismuth are very easily hydrolyzed in the aqueous solution. The aqueous solution reaction preparation for some complexes of bismuth is very difficult [25, 26]. In this paper, we report the syntheses and characterization of the two ternary bismuth(III) complexes of phthalic acid.

## EXPERIMENTAL SECTION

**Materials and physical measurements**

In addition to *L*-cystine (*L*-H<sub>2</sub>cys) was biochemical reagent, other chemicals used in the experiments were analytical reagents as received from commercial sources and without further purification. *L*-cystine and manna sugar were purchased from Sinopharm Chemical Reagent Co., Ltd., while phthalic acid (H<sub>2</sub>phth), lithium hydroxide (LiOH·H<sub>2</sub>O) and bismuth nitrate [Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O] were received from Chengdu Kelong Chemical Reagent Company.

The contents of carbon, hydrogen, nitrogen, sulfur and oxygen in the complexes were determined by Vario EL CUBE elemental analyzer for Germany Elemental Analysis System Company. The content of bismuth in the complexes was determined by EDTA complexometric titration. The X-ray powder diffraction patterns of the complexes were recorded by a D/max-II X-ray diffractometer in the diffraction angle range of 3°–80° from Japan Science Corporation, Cu K<sub>α1</sub> radiation ( $\lambda = 0.154056$  nm), Ni filter, scanning rate was 8°(2 $\theta$ ) min<sup>-1</sup> at room temperature. The Infrared spectra of the complexes and phthalic acid were measured by a Nicolet 5700 Fourier transform infrared spectrometer from America using potassium bromide pellets in the region of 4000–400 cm<sup>-1</sup>. The thermogravimetric analyses for the complexes were performed by a TA Q500 thermal analyzer in dry nitrogen at a heating rate of 10 °C min<sup>-1</sup>.

**Synthesis of phthalate lithium**

Phthalic acid (10 mmol, 1.66 g) and lithium hydroxide (20 mmol, 0.84 g) were weighed and mixed in aqueous solution. The mixture was stirred for 4 h at room temperature. The solvent was evaporated by the rotary evaporator, and the resultant was filtrated and dried about 24 h in the vacuum drying oven at 40 °C. Lastly, the white powder of phthalate lithium (Li<sub>2</sub>phth) was obtained.

**Synthesis of complex Bi(phth)(NO<sub>3</sub>)·4H<sub>2</sub>O**

2 mmol (0.97 g) bismuth nitrate [Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O] and 2 mmol (0.36 g) manna sugar were placed in an agate mortar and pestle to a paste. Then the mixture was dissolved in 40 mL deionized water, and the colorless and transparent solution was obtained. Afterwards 20 mL aqueous solution of Li<sub>2</sub>phth (2.0 mmol, 0.36 g) was added to the above solution, the mixed solution was continuously stirred at room temperature for 5 h. Finally, the resultant was filtered by vacuum and dried in a vacuum drying oven at 40 °C for 24 h. The resultant of white powder was obtained, and the yield was about 85%.

**Synthesis of complex Bi(phth)(*L*-cys)<sub>0.5</sub>·H<sub>2</sub>O**

2 mmol (0.97 g) bismuth nitrate and 2 mmol (0.36 g) manna sugar were placed in an agate mortar and pestle to a paste, then the mixture was dissolved in 40 mL deionized water, and became the colorless and transparent solution. Afterwards the 20 mL aqueous solution of phthalic acid (2 mmol, 0.33 g), *L*-cystine (1 mmol, 0.24 g) and lithium hydroxide (6 mmol, 0.25 g) was added to the above solution, the mixed solution was continuously stirred at room temperature for 5 h. Finally, the resultant was filtered by vacuum and dried in a vacuum drying oven at 40 °C for 24 h. The resultant of white powder was obtained, and the yield was about 78%.

## RESULTS AND DISCUSSION

**The composition of the complexes**

The elemental analyses results of the complexes are listed in Table 1. The composition formulae of the complexes are BiC<sub>8</sub>H<sub>12</sub>O<sub>11</sub>N (*M<sub>r</sub>* = 507.16) and BiC<sub>11</sub>H<sub>11</sub>O<sub>7</sub>NS (*M<sub>r</sub>* = 510.24), respectively. The calculated results of mass fraction of each element in the complexes are very close to the experimental ones. Therefore, combined with the results of the infrared spectra and the thermal analysis, the molecular formulae of the complexes is Bi(phth)(NO<sub>3</sub>)·4H<sub>2</sub>O and Bi(phth)(*L*-cys)<sub>0.5</sub>·H<sub>2</sub>O, respectively.

Table 1 Elemental analyses results of the complexes (Calculated values are in brackets)

Complex	Formula	w(Bi)(%)	w(C)(%)	w(H)(%)	w(N)(%)	w(S)(%)	w(O)(%)
Bi(phth)(NO <sub>3</sub> )·4H <sub>2</sub> O	BiC <sub>8</sub> H <sub>12</sub> O <sub>11</sub> N	41.55 (41.21)	19.11 (18.95)	2.31 (2.38)	2.49 (2.76)	–	34.22 (34.70)
Bi(phth)( <i>L</i> -cys) <sub>0.5</sub> ·H <sub>2</sub> O	BiC <sub>11</sub> H <sub>11</sub> O <sub>7</sub> NS	40.56 (40.96)	26.01 (25.89)	2.23 (2.17)	2.84 (2.74)	6.39 (6.28)	21.97 (21.95)

**X-ray powder diffraction analysis**

Figs. 1 and 2 depict the XRD patterns of the complexes Bi(phth)(NO<sub>3</sub>)·4H<sub>2</sub>O and Bi(phth)(*L*-cys)<sub>0.5</sub>·H<sub>2</sub>O. It is seen that the complexes of Bi(phth)(NO<sub>3</sub>)·4H<sub>2</sub>O at 2 $\theta$  = 8.02°, 25.92° and 16.03°, and Bi(phth)(*L*-cys)<sub>0.5</sub>·H<sub>2</sub>O at 2 $\theta$  = 28.51°, 11.68° and 27.79°, respectively, produce the three strong peaks, while the three strong peaks of the reactants of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (JCPDS card no. 12-0148) at 2 $\theta$  = 16.14°, 15.62° and 10.71°, and phthalic acid (JCPDS card no.

13-0823) at  $2\theta = 15.45^\circ$ ,  $27.08^\circ$  and  $22.32^\circ$ , and *L*-H<sub>2</sub>cys (JCPDS card no. 23-1663) at  $2\theta = 28.50^\circ$ ,  $18.84^\circ$  and  $28.00^\circ$  disappear in the complexes. The diffraction angle ( $2\theta$ ), spacing ( $d$ ) and diffractive intensity of the products are different from the reactive materials, which may explain that the above two products are not simple mixing of the reactants, but the formation of new compounds.

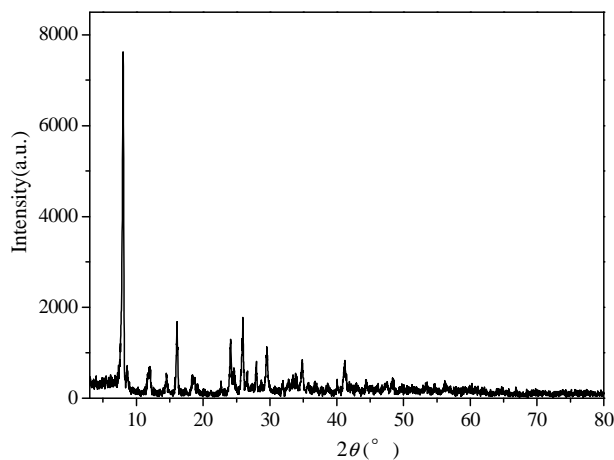


Fig. 1 XRD pattern of the complex  $\text{Bi}(\text{phth})(\text{NO}_3)\cdot 4\text{H}_2\text{O}$

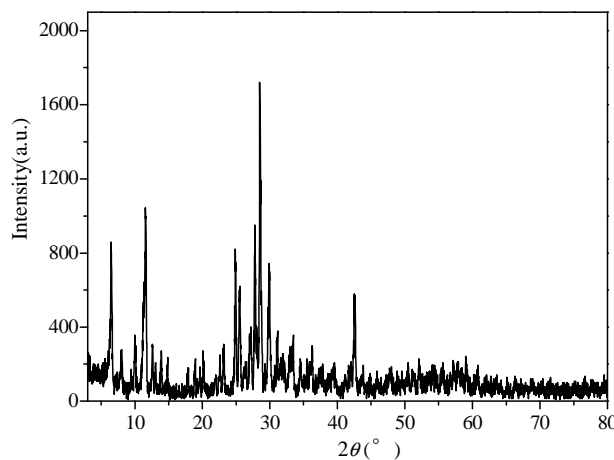


Fig. 2 XRD pattern of the complex  $\text{Bi}(\text{phth})(\text{L-cys})_{0.5}\cdot \text{H}_2\text{O}$

Table 2 Experimental data and calculated results for powder X-ray diffraction pattern of the complex of  $\text{Bi}(\text{phth})(\text{NO}_3)\cdot 4\text{H}_2\text{O}$  (monoclinic:  $a = 1.0792$  nm,  $b = 2.2169$  nm,  $c = 1.0306$  nm and  $\beta = 95.68^\circ$ )

$2\theta(^\circ)$	$h$	$k$	$l$	$d_{\text{exp}}(\text{nm})$	$d_{\text{cal}}(\text{nm})$	$I/I_0$	$2\theta(^\circ)$	$h$	$k$	$l$	$d_{\text{exp}}(\text{nm})$	$d_{\text{cal}}(\text{nm})$	$I/I_0$
8.02	1	0	0	1.0737	1.0739	100.0	25.92	3	1	-1	0.3434	0.3446	21.9
8.62	0	0	1	1.0252	1.0255	7.4	26.63	1	6	-1	0.3345	0.3340	4.2
11.74	0	2	1	0.7530	0.7528	5.6	27.96	2	3	2	0.3189	0.3191	8.3
12.00	1	1	-1	0.7368	0.7369	7.5	29.54	2	0	-3	0.3021	0.3022	13.1
14.50	1	3	0	0.6103	0.6088	6.1	33.48	1	5	-3	0.2674	0.2675	3.8
16.03	0	4	0	0.5526	0.5542	21.3	33.82	1	7	-2	0.2648	0.2646	4.6
18.40	1	0	-2	0.4817	0.4816	5.7	34.56	4	2	-1	0.2593	0.2589	2.2
22.68	2	0	-2	0.3917	0.3907	1.7	34.84	3	6	0	0.2573	0.2571	9.0
24.12	2	2	-2	0.3687	0.3684	15.3	35.02	0	0	4	0.2560	0.2564	3.6
24.53	1	4	-2	0.3627	0.3635	6.9	40.93	4	5	1	0.2203	0.2202	3.6
25.63	1	4	2	0.3474	0.3474	6.4	41.08	1	9	-2	0.2195	0.2193	5.9

Table 3 Experimental data and calculated results for powder X-ray diffraction pattern of the complex of  $\text{Bi}(\text{phth})(\text{L-cys})_{0.5}\cdot \text{H}_2\text{O}$  (monoclinic:  $a = 1.4183$  nm,  $b = 2.2633$  nm,  $c = 1.3753$  nm and  $\beta = 96.49^\circ$ )

$2\theta(^\circ)$	$h$	$k$	$l$	$d_{\text{exp}}(\text{nm})$	$d_{\text{cal}}(\text{nm})$	$I/I_0$	$2\theta(^\circ)$	$h$	$k$	$l$	$d_{\text{exp}}(\text{nm})$	$d_{\text{cal}}(\text{nm})$	$I/I_0$
6.23	1	0	0	1.4105	1.4092	17.5	27.79	1	1	4	0.3207	0.3205	48.9
6.56	0	1	0	1.3665	1.3665	46.6	28.51	3	5	1	0.3128	0.3116	100.0
9.85	1	2	0	0.8848	0.8824	17.5	28.81	3	0	3	0.3102	0.3100	31.1
11.68	1	2	-1	0.7657	0.7664	59.5	30.81	0	6	3	0.2907	0.2905	5.6
12.53	2	0	0	0.7028	0.7046	14.3	31.17	3	3	3	0.2870	0.2867	16.5
14.83	2	2	0	0.5961	0.5981	11.2	31.69	0	8	0	0.2828	0.2829	8.8
17.80	1	4	-1	0.4978	0.4972	6.7	32.06	5	1	0	0.2793	0.2797	9.4
18.90	2	3	1	0.4680	0.4692	10.9	32.78	5	2	-1	0.2738	0.2740	11.5
19.68	0	5	0	0.4522	0.4527	7.1	33.16	0	1	-5	0.2714	0.2713	14.3
20.37	1	1	-3	0.4397	0.4400	3.0	33.43	4	5	1	0.2676	0.2678	18.7
23.06	2	4	-2	0.3837	0.3832	16.0	34.46	3	4	-4	0.2597	0.2598	11.0
24.86	3	4	-1	0.3575	0.3572	46.6	42.38	5	7	-1	0.2126	0.2127	30.9
25.20	4	0	-1	0.3509	0.3509	14.7	50.41	5	6	4	0.1811	0.1812	8.4
25.52	1	6	1	0.3493	0.3496	32.0	52.10	1	5	7	0.1755	0.1754	8.6
26.93	3	4	-2	0.3314	0.3316	16.8	55.61	6	8	-4	0.1657	0.1658	8.4
27.21	2	3	3	0.3278	0.3280	27.2	59.06	5	8	-6	0.1564	0.1565	9.9

Getting the index calculation of XRD data base on the computer program of least squares method [24], and the results are shown in Tables 2 and 3. As is shown in Tables 2 and 3, all the peaks in the powder X-ray diffraction of the complexes can be very well indexed by a set of lattice parameters according to monoclinic system, and the maximum relative deviations between the experimental and calculated spacing  $d$  are less than 0.4%. The results show that the resultants are all single phase compounds. The crystal structures of the complexes belong to monoclinic system with crystal cell parameters of  $a = 1.0792$  nm,  $b = 2.2169$  nm,  $c = 1.0306$  nm and  $\beta = 95.68^\circ$  for

$\text{Bi}(\text{phth})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and  $a = 1.4183 \text{ nm}$ ,  $b = 2.2633 \text{ nm}$ ,  $c = 1.3753 \text{ nm}$  and  $\beta = 96.49^\circ$  for  $\text{Bi}(\text{phth})(L\text{-cys})_{0.5} \cdot \text{H}_2\text{O}$ , respectively.

### Infrared spectra

The IR spectra of the complexes are compared with those of free ligand in order to determine the coordination sites that may be involved in chelation. The IR spectra of the ligand and the complexes are shown in Fig. 3. The IR spectra of  $\text{Bi}(\text{phth})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Bi}(\text{phth})(L\text{-cys})_{0.5} \cdot \text{H}_2\text{O}$  show that the broad strong absorption band at  $3439 \text{ cm}^{-1}$  or  $3442 \text{ cm}^{-1}$  is due to the  $\nu(\text{O-H})$  of water molecules, absorption band at  $3059 \text{ cm}^{-1}$  is due to  $\nu(\text{N-H})$  of *L*-cystine, respectively. The absorption peak at  $1628 \text{ cm}^{-1}$  or  $1624 \text{ cm}^{-1}$  is assigned to the deformation vibration of water molecules [15]. The stretching vibration peaks of  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  are observed at  $1688 \text{ cm}^{-1}$  and  $1406 \text{ cm}^{-1}$  for free phthalic acid ligand. The strong absorption band at  $1546 \text{ cm}^{-1}$  is assigned to the asymmetric stretching vibration of carboxylic groups while the absorption band at  $1394 \text{ cm}^{-1}$  corresponds to the symmetric stretching vibration of carboxylic groups for IR spectra of  $\text{Bi}(\text{phth})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . Usually, the difference value ( $\Delta\nu$ ) between  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  in the IR spectra can be used to derive information regarding the bonding modes of carboxylic anions. Namely, the  $\Delta\nu$  of  $152 \text{ cm}^{-1}$  indicates that the carboxylic groups in the complex  $\text{Bi}(\text{phth})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  exhibit bidentate bridge type coordination mode [21]. The free nitrate radical belongs to  $D_{3h}$  symmetry group. Many vibration modes in the molecule with  $D_{3h}$  symmetry are infrared active. When the oxygen atoms of nitrate radical are coordinated to the metal ions, its symmetry group is changed from  $D_{3h}$  to  $C_{2v}$ . The vibration bands at  $1504$ ,  $1094$ ,  $767$  and  $706 \text{ cm}^{-1}$  are attributed to the characteristic absorption peaks of the coordinated  $\text{NO}_3^-$ . The characteristic vibration band at *ca.*  $700 \text{ cm}^{-1}$  is split into two absorption peaks of  $767$  and  $706 \text{ cm}^{-1}$ , and the difference value is  $61 \text{ cm}^{-1}$ , the difference range of  $66\text{--}25 \text{ cm}^{-1}$  shows bidentate coordinated nitrate. The new bands at  $585$  and  $473 \text{ cm}^{-1}$  are found in the infrared spectrum of the complexes, which are assigned to the stretching vibration peaks of the Bi-O bonds which are formed with the nitrate-O and carboxylate-O atoms, respectively. Therefore, it is concluded that phthalate behaves as bidentate mode and binds to the bismuth ions through the nitrate oxygen atoms and carboxylate oxygen atoms in the deprotonated carboxyl groups [27]. The infrared spectrum of the complex  $\text{Bi}(\text{phth})(L\text{-cys})_{0.5} \cdot \text{H}_2\text{O}$  exhibits salient features at  $1582$  and  $1384 \text{ cm}^{-1}$ , which are assigned to the  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  stretching vibration peaks of the coordinated carboxyl groups ( $\Delta\nu[\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)] = 198 \text{ cm}^{-1}$ ), it indicates that the oxygen atoms of the carboxyl in the compound is directly linked with the bismuth ion and the presence of carboxylate groups coordinate to bismuth ion in bidentate bridge type coordination mode [28-30]. The medium strong bands at  $569$  and  $462 \text{ cm}^{-1}$  are attributed to the Bi-O bond stretching vibration peaks.

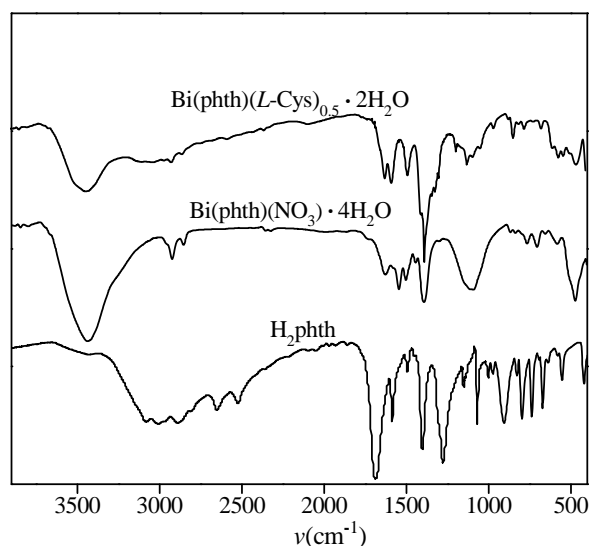


Fig. 3 Infrared spectra of the ligand and the complexes

### Thermal decomposition process

The TG-DTG curves are made in order to verify the bonds and composition of complexes [31]. The thermal stability of the complexes were examined representatively by thermogravimetric analysis (TG) in nitrogen atmosphere from room temperature to  $500 \text{ }^\circ\text{C}$  at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ . The results are shown in Figs. 4 and 5, the data of possible thermal decomposition processes are listed in Table 4. The TG curve of the two complexes display three main steps of mass loss. Fig. 4 shows, the first mass loss of  $14.08\%$  in TG curve occurs between  $50 \text{ }^\circ\text{C}$  and  $190 \text{ }^\circ\text{C}$  in the complex  $\text{Bi}(\text{phth})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , corresponding to the loss of four water molecules. The theoretical mass loss ( $14.21\%$ ) of water molecules is much closed to experimental mass loss. The second mass loss of the complex from  $190\text{--}290 \text{ }^\circ\text{C}$  is observed *ca.*  $10.72\%$ , and it is due to the elimination of nitrate radical that decomposed into  $\text{NO}_2$  and

O<sub>2</sub> from the complex, the experimental mass loss is close to the calculated one (10.65%). Upon further heating, the mass loss of 29.14% in TG curve corresponds to oxidation and decomposition of the phthalate ligand (calculated 29.20%). The mass loss remains constant until *ca.* 460 °C, and the final residue is only bismuthous oxide, and the experimental result (46.06%) is in agreement with the result of theoretical calculation (45.94%). These results further ascertain that the complex is composed of Bi(phth)(NO<sub>3</sub>)·4H<sub>2</sub>O.

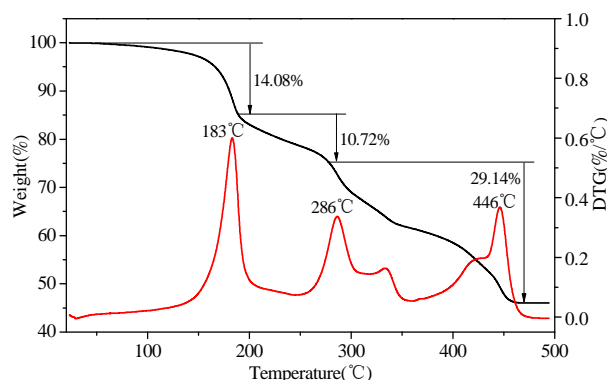


Fig. 4 TG-DTG curves of Bi(phth)(NO<sub>3</sub>)·4H<sub>2</sub>O

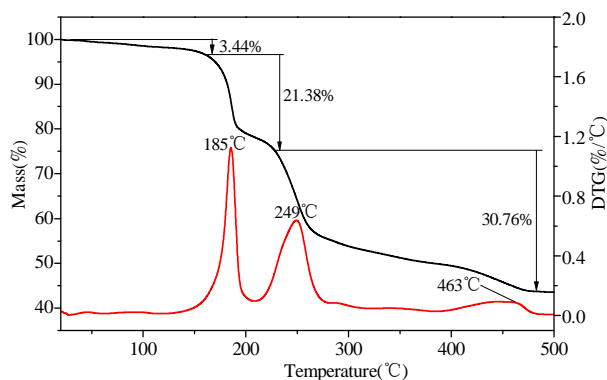


Fig. 5 TG-DTG curves of Bi(phth)(L-cys)<sub>0.5</sub>·H<sub>2</sub>O

Fig. 5 shows that one water molecule is lost when heating the compound from 40 °C to 170 °C. This accounts for 3.44% mass loss observed in TG curve. The theoretical mass loss (3.53%) of water molecule is much closed to the experimental mass loss. The second mass loss of the complex Bi(phth)(L-cys)<sub>0.5</sub>·H<sub>2</sub>O occurs between 170 °C and 230 °C. It is due to the elimination of L-cystine anion ligand. The experimental mass loss of 21.38% is close to the calculated one (21.78%). Upon further heating, the complex is decomposed completely until *ca.* 480 °C, the mass loss of 30.57% in TG curve corresponds to oxidation and decomposition of the phthalate ligand (calculated 29.03%). The final residue is bismuthous oxide, and the experimental result (44.61%) is in agreement with the result of theoretical calculation (45.66%). These results further ascertain the complex is composed of Bi(phth)(L-cys)<sub>0.5</sub>·H<sub>2</sub>O.

Table 4 Thermal decomposition data of the complexes Bi(phth)(NO<sub>3</sub>)·4H<sub>2</sub>O and Bi(phth)(L-cys)<sub>0.5</sub>·H<sub>2</sub>O

Reaction	Peak Temp. in DTG (°C)	Mass loss (%)	
		<i>m</i> <sub>exp</sub>	<i>m</i> <sub>theor</sub>
Bi(phth)(NO <sub>3</sub> )·4H <sub>2</sub> O			
↓ -4H <sub>2</sub> O	183	14.08	14.21
Bi(phth)(NO <sub>3</sub> )			
↓ -NO <sub>2</sub> , -0.25O <sub>2</sub>	286	10.72	10.65
0.5Bi <sub>2</sub> (phth) <sub>2</sub> O			
↓ -C <sub>6</sub> H <sub>4</sub> (CO) <sub>2</sub> O	446	29.14	29.20
0.5Bi <sub>2</sub> O <sub>3</sub>		46.06 <sup>a</sup>	45.94 <sup>b</sup>
Bi(phth)(L-cys) <sub>0.5</sub> ·H <sub>2</sub> O			
↓ -H <sub>2</sub> O	185	3.44	3.53
Bi(phth)(L-cys) <sub>0.5</sub>			
↓ -0.5[SCH <sub>2</sub> CH(NH <sub>2</sub> )CO] <sub>2</sub> O	249	21.38	21.78
0.5Bi <sub>2</sub> (phth) <sub>2</sub> O			
↓ -C <sub>6</sub> H <sub>4</sub> (CO) <sub>2</sub> O	463	30.57	29.03
0.5Bi <sub>2</sub> O <sub>3</sub>		44.61 <sup>a</sup>	45.66 <sup>b</sup>

<sup>a</sup> The experimental mass% of the residue in the sample, <sup>b</sup> the calculated mass% of the residue in the sample.

## CONCLUSION

Two ternary complexes of bismuth(III) were synthesized with bismuth nitrate, phthalic acid and L-cystine as main raw materials by liquid reaction at room temperature. The composition of complexes was determined by titration analysis and elemental analyses, and the structure of complexes was characterized by XRD, FTIR and TG-DTG. The crystal structures of the two complexes belong to monoclinic system, and the lattice parameters are: *a* = 1.0792 nm, *b* = 2.2169 nm, *c* = 1.0306 nm and  $\beta$  = 95.68° for Bi(phth)(NO<sub>3</sub>)·4H<sub>2</sub>O, and *a* = 1.4183 nm, *b* = 2.2633 nm, *c* = 1.3753 nm and  $\beta$  = 96.49° for Bi(phth)(L-cys)<sub>0.5</sub>·H<sub>2</sub>O, respectively. The results demonstrate that the carboxy group oxygen atoms of phthalate and L-cystine and the oxygen atoms from nitrate are coordinated directly to bismuth(III) ion in the two complexes. The complexes are decomposed into Bi<sub>2</sub>O<sub>3</sub> at about 480 °C.

## Acknowledgments

This work is supported by the Scientific Research Funds of Sichuan Provincial Education Department in China (10ZA016). The authors are very grateful to Analytical Testing Center of Southwest University of Science and

Technology, and Engineering Research Center of Biomass Materials of Education Ministry for the testing of elemental analyses, XRD, FTIR and TG-DTG.

## REFERENCES

- [1] S Sivasekar; K Ramalingam; C Rizzoli; N Alexander, *Inorg. Chim. Acta*, **2014**, 419, 82–88.
- [2] V Stavila; RL Davidovich; A Gulca; KH Whitmire, *Coord. Chem. Rev.*, **2006**, 250(21-22), 2782–2810.
- [3] MX Li; M Yang; JY Niu; LZ Zhang; SQ Xie, *Inorg. Chem.*, **2012**, 51(22), 12521–12526.
- [4] TD Boyd; I Kumar; EE Wagner; KH Whitmire, *Chem. Commun.*, **2014**, 50(27), 3556–59.
- [5] KG Caulton; LG Hubcrt-pfalzgraf, *Chem. Rev.*, **1990**, 90(6), 969–995.
- [6] GQ Zhong; SR Luan; P Wang; YC Guo; YR Chen; YQ Jia, *J. Therm. Anal. Calorim.*, **2006**, 86(3), 775–781.
- [7] LE Turner; MG Davidson; MD Jones; H Ott; VS Schulz; PJ Wilson, *Inorg. Chem.*, **2006**, 45(16), 6123–6125.
- [8] ZP Zhang; GQ Zhong; QY Jiang, *Prog. Chem.*, **2008**, 20(9), 1315–1323.
- [9] JG Shao; YX Yang; BW Li; LP Zhang; YR Chen; XL Liu, *J. Therm. Anal. Calorim.*, **2009**, 96(1), 277–285.
- [10] QY Jiang; J Shen; GQ Zhong, *Prog. Chem.*, **2006**, 18(12), 1634–1645.
- [11] M Busse; I Trinh; PC Junk; RL Ferrero; PC Andrews, *Chem.-Eur. J.*, **2013**, 19(17), 5264–5275.
- [12] JA Lessa; DC Reis; IC Mendes; NL Speziali; LF Rocha; VRA Pereira; CML Melo; H Beraldo, *Polyhedron*, **2011**, 30(2), 372–380.
- [13] DC Reis; MCX Pinto; EM Souza-Fagundes; SM Wardell; JL Wardell; H Beraldo, *Eur. J. Med. Chem.*, **2010**, 45(9), 3904–3910.
- [14] II Ozturk; CN Banti; N Kourkoumelis; MJ Manos; AJ Tasiopoulos; AM Owczarzak; M Kubicki; SK Hadjikakou, *Polyhedron*, **2014**, 67, 89–103.
- [15] QY Jiang; HQ Deng; YM Hu; J Shen; GQ Zhong; NH Hu, *Acta Chim. Sin.*, **2008**, 66(12), 1429–1434.
- [16] EV Kovaleva; LA Zemnukhova; VM Nikitin; RL Davidovich; UV Kharchenko, *Russ. J. Appl. Chem.*, **2003**, 76(9), 1389–1392.
- [17] XW Zhang; J Xia; HW Yan; SL Luo; SF Yin; CT Au; WY Wong, *J. Organomet. Chem.*, **2009**, 694(18), 3019–3026.
- [18] SV Kharitonov; YuM Kozyreva; VI Zarembo, *Pharm. Chem. J.*, **2008**, 42(10), 604–606.
- [19] YK Li; M Yang; MX Li; H Yu; HC Wu; SQ Xie, *Bioorg. Med. Chem. Lett.*, **2013**, 23(8), 2288–2292.
- [20] HZ Sun; KY Szeto, *J. Inorg. Biochem.*, **2003**, 94(1-2), 114–120.
- [21] GQ Zhong; J Shen; QY Jiang; YQ Jia; MJ Chen; ZP Zhang, *J. Therm. Anal. Calorim.*, **2008**, 92(2), 607–616.
- [22] QY Jiang; GQ Zhong; J Shen, *Chin. J. Chem.*, **2011**, 29(12): 2637–2642.
- [23] J Shen; B Jin; QY Jiang; GQ Zhong; YM Hu; JC Huo, *Inorg. Chim. Acta*, **2012**, 385, 158–163.
- [24] D Li; GQ Zhong, *Bioinorg. Chem. Appl.*, **2014**, 2014, Article ID 461605.
- [25] GQ Zhong; RR Jia; YQ Jia, *Adv. Mater. Res.*, **2012**, 549, 292–296.
- [26] M Gu; GQ Zhong, *J. Synth. Cryst.*, **2013**, 42(6), 1241–1246.
- [27] MS Refat; GG Mohamed; RF de Farias; AK Powell; MS El-Garib; SA El-Korashy; MA Hussien, *J. Therm. Anal. Calorim.*, **2010**, 102(1), 225–232.
- [28] GB Deacon; R J Philips, *Coord. Chem. Rev.*, **1980**, 33(3), 227–250.
- [29] K Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edition, Wiley & Sons, New York, **1986**.
- [30] B Xu; B Yan, *Spectrosc. Lett.*, **2006**, 39(3), 237–248.
- [31] D Li; M Gu; GQ Zhong, *J. Synth. Cryst.*, **2013**, 42(12), 2726–2731.