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SYNTHESIS, CHARACTERIZATION AND THERMAL DECOMPOSITION OF THIOUREA COMPLEXES OF ANTIMONY AND BISMUTH TRIIODIDE

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The thiourea complexes of antimony and bismuth triiodide were synthesized by a direct reaction of antimony and bismuth triiodide with thiourea powder at room temperature. The formula of the complex is $MI_3[SC(NH_2)_2]_3$(M=Sb, Bi). The crystal structure of the complexes belongs to monoclinic system and the lattice parameters are a=1.4772 nm, b=1.6582 nm, c=2.0674 nm and β=90.81° for $SbI_3(SC(NH_2)_2)_3$ and a=1.4009 nm, b=2.0170 nm, c=2.0397 nm and β=90.84° for $BiI_3[SC(NH_2)_2]_3$. The infrared spectra reveal that the trivalent antimony or bismuth ion is coordinated by the nitrogen atom, not the sulfur atom of the thiourea. Thermal analysis shows that there are two times structure rearrangements or phase transformation in the complexes from 100 to 170°C.

Keywords: *characterization, solid–solid synthesis, thermal decomposition, thiourea complex of Sb and Bi*

Introduction

Solid–solid reaction is a simple synthetic method and has been used in inorganic synthesis. The solid complexes of transition metal ions and various organic ligands were synthesized through solid–solid reaction [1]. By comparison, the solid complexes of main group metal ions are less reported [2–4]. Especially, the solid–solid reaction synthesis of complexes of antimony and bismuth is rare. The complexes of some main group elements [5], such as antimony and bismuth, can possess a certain biological function [6–8]. To synthesize new complexes of antimony and bismuth will be interesting not only for main group element chemistry, but also bioinorganic chemistry. Since many inorganic salts of antimony and bismuth are easily hydrolyzed in aqueous solution [9], to synthesize solid complexes of antimony or bismuth through reaction in aqueous solution may be difficult. However, such complexes can be easily prepared by solid–solid reaction [10, 11]. Here, we report a solid–solid reaction synthetic process of the thiourea complexes of antimony and bismuth triiodide, the results of indexing to the powder X-ray diffraction patterns of the complexes, their far-infrared spectra and thermal decomposition.

Experimental

Antimony triiodide, bismuth triiodide and thiourea used in the experiments are analytical grade reagents. Synthesis of the thiourea complex of antimony triiodide: First, 2.0880 g (4.155 mmol) SbI_3 and 0.9489 g (12.47 mmol) $SC(NH_2)_2$ were weighed and well mixed. With careful grinding in an agate mortar, the mixture's color was red at first, then gradually became yellow. The mixture was kept being grounded at room temperature for about 2 h, then dried in a vacuum desiccator over phosphorus pentoxide for a week. The product was a yellow powder and does not absorb moisture in the air. Synthesis of the thiourea complex of bismuth triiodide: 1.9962 g (3.385 mmol) BiI_3 and 0.7731 g (10.156 mmol) $SC(NH_2)_2$ were weighed. Then, the synthetic process was performed according to the above-mentioned procedure. At first, no reaction was observed. After adding a few of absolute methanol, the black mixture turned red. After drying, a red powder was obtained, which does not absorb moisture.

The powder X-ray diffraction patterns for the products were recorded by a D/max-YB X-ray diffractometer, $CuK_{\alpha 1}$ radiation at room temperature. The results of indexing to the powder X-ray diffraction patterns are shown in Tables 1 and 2. The far-infrared spectra of the complexes and thiourea were recorded by a Nicolet 5D-FT spectrometer and potassium bromide disk technique. The far-infrared spectra are shown in Fig. 1.

Thermal studies were performed by SDT Q600 V5.0 Thermal Analyzer (Simultaneous DSC-TGA Q Series, TA Instruments, US.), in the air, with a heating rate of 10°C min^{-1}, the reference α-Al_2O_3. The sample mass was 4.976 mg for the complex of antimony and 2.292 mg for that of bismuth. The TG and

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Table 1 The experimental and calculated results for powder X-ray diffraction pattern of $SbI_3[SC(NH_2)_2]_3$. (Monoclinic: *a*=1.4772 nm, *b*=1.6582 nm, *c*=2.0674 nm, β=90.81°)

h, *k*, *l*	d_{exp}/nm	d_{cal}/nm	I/I_0	*h*, *k*, *l*	d_{exp}/nm	d_{cal}/nm	I/I_0
102	0.8418	0.8413	14	–451	0.2457	0.2453	15
–201	0.6986	0.6986	61	–263	0.2428	0.2427	10
210	0.6743	0.6746	40	056	0.2389	0.2389	12
022	0.6458	0.6467	100	–362	0.2351	0.2351	24
030	0.5528	0.5527	12	–337	0.2313	0.2314	10
004	0.5163	0.5168	24	–238	0.2240	0.2240	12
014	0.4935	0.4934	43	–265	0.2200	0.2199	16
–302	0.4471	0.4470	19	–157	0.2185	0.2185	13
–231	0.4350	0.4335	22	–347	0.2171	0.2171	14
124	0.4191	0.4191	21	–633	0.2147	0.2146	14
115	0.3854	0.3858	25	437	0.2115	0.2116	12
330	0.3672	0.3676	44	–634	0.2072	0.2072	13
–411	0.3562	0.3559	25	712	0.2048	0.2046	15
143	0.3448	0.3448	39	–281	0.1987	0.1987	29
–225	0.3329	0.3325	11	419	0.1925	0.1925	18
116	0.3281	0.3279	21	–448	0.1897	0.1895	13
–422	0.3220	0.3219	57	–572	0.1822	0.1822	19
413	0.3175	0.3176	58	376	0.1810	0.1810	13
–152	0.3095	0.3091	46	–368	0.1768	0.1769	9
–342	0.3037	0.3039	87	–169	0.1757	0.1756	9
–501	0.2930	0.2930	42	–391	0.1720	0.1720	8
145	0.2864	0.2866	9	–619	0.1682	0.1683	12
–316	0.2800	0.2801	15	851	0.1607	0.1607	7
–127	0.2741	0.2741	27	–680	0.1585	0.1586	12
326	0.2656	0.2656	23	578	0.1497	0.1497	8
–227	0.2614	0.2615	17	595	0.1459	0.1459	7
–137	0.2574	0.2571	18	598	0.1332	0.1333	8
163	0.2525	0.2525	27	–599	0.1296	0.1297	8

DTA curves of the complexes are shown in Fig. 2. The possible thermal decomposition processes, the experimental and calculated results for the thermal analysis are summarized in Table 3. To check the pyrolysis reactions, the relative contents of Sb and Bi in the intermediates were also determined. First, a certain amount (253.5 mg) of the Sb complex or that (207.9 mg) of the Bi complex was placed in an alumina crucible and heated in a muffle furnace. After the furnace temperature rose to a corresponding temperature, the sample was kept in the furnace for 10 min. The mass loss of the sample was measured and about 50 mg pyrolysis product was taken to determine the relative content of Sb or Bi in the product. Antimony was determined by iodimetry and bismuth by EDTA and the standard zinc chloride solution back titration, respectively. Then, the residual product in the alumina crucible was heated at another corresponding temperature for 10 min followed by repeating the above procedure. The intermediates in three steps of the thermal decomposition process of the complex were analyzed. The analysis results are given in Table 3.

Results and discussion

The indexing to the powder X-ray diffraction patterns of the resultants shows that all the diffraction peaks in each pattern can be readily indexed by a set of lattice parameters according to monoclinic system. As Tables 1 and 2 show, the largest relative deviation between the calculated and measured spacing is less than 0.3%. This indicates that the resultant is a single

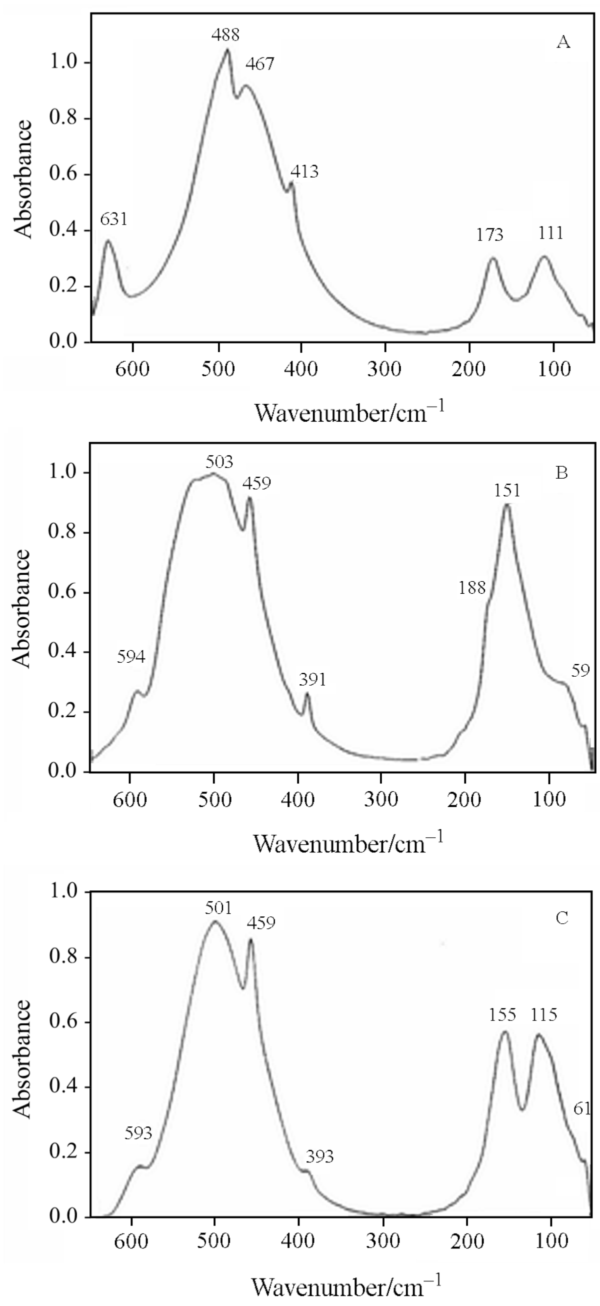

Fig. 1 The far-infrared spectra of A – $SC(NH_2)_2$; B – $SbI_3[SC(NH_2)_2]_3$; C – $BiI_3[SC(NH_2)_2]_3$

phase compound with monoclinic symmetry. The crystal structure of antimony and bismuth triiodide belongs to hexagonal system (JCPDS7-273 and 7-269). Thiourea belongs to orthorhombic system (JCPDS31-1934). However, the crystal structure of the resultants belongs to neither the hexagonal system nor the orthorhombic system, but the monoclinic system. Besides, the color of the resultants are also very different from that of the reactants. Obviously, the resultants must be new compounds.

Some stable complexes composed of transition metal salt and thiourea are known [12]. The coordination number of the trivalent antimony and bismuth ion can be six [9]. Therefore, the trivalent antimony or bismuth ion can also be coordinated by three donor atoms from the thiourea, except for three iodine anions. Thiourea can coordinate to the metal ion through either the sulfur or the nitrogen atom. In most cases, the metal ion is coordinated by the sulfur atom. Only in a few metal thiourea complexes [13, 14], the metal ion is coordinated by the nitrogen atom. IR spectra can distinguish which donor atom (sulfur or nitrogen atom) coordinates to the metal ion. If the metal ion is coordinated by the sulfur atom, there must be the absorption peak from the stretching vibration of the M–S bond in 200–300 cm^{-1} region [14]. As Fig. 1 shows, in the infrared spectrum of thiourea, the absorption peak at 488 (or 467 cm^{-1}) can be assigned to the N–C–N deformation vibration, 413 cm^{-1} to the N–C–S deformation vibration, and 631 cm^{-1} to the C=S rocking vibration [12]. The absorption peaks at 173 and 111 cm^{-1} are from the lattice vibration in the thiourea [15]. There is no absorption peaks from 200 to 300 cm^{-1} in the infrared spectra of the complexes. This is an important evidence for the absence of the Sb–S and Bi–S bond. This demonstrates that the thiourea molecule coordinates to the antimony or bismuth ion through the nitrogen atom. We find that the main peaks in the infrared spectrum of the thiourea also appear in the infrared spectrum of the complexes, but some peaks shift. For example, in the antimony complex, the N–C–N deformation vibration shifts from 488 cm^{-1} (or 467 cm^{-1}) to 503 cm^{-1} (or 459 cm^{-1}), the N–C–S deformation vibration shifts from 413 to 391 cm^{-1} and the C=S rocking vibration shifts from 631 to 594 cm^{-1}, and in the bismuth complex, the N–C–N deformation vibration shifts from 488 cm^{-1} (or 467 cm^{-1}) to 501 cm^{-1} (or 459 cm^{-1}), the N–C–S deformation vibration shifts from 413 to 393 cm^{-1} and the C=S rocking vibration shifts from 631 to 593 cm^{-1}. The shifts can be attributed to the coordination between the antimony or bismuth ion and the nitrogen atom of thiourea. The formation of the coordination bond between the antimony or bismuth ion and the nitrogen atom must affect the bonding between the nitrogen and carbon atom in the thiourea and lead to the variation of the vibration frequency of the chemical bonds containing the carbon and nitrogen atom. In the IR spectra of the gaseous molecule of the antimony triiodide (or bismuth triiodide), there are 4 absorption peaks: u_s=186.5 cm^{-1} (or 145.8 cm^{-1}) and u_{as}=147 cm^{-1} (or 115.2 cm^{-1}) from the symmetric and antisymmetric stretching vibration of the Sb–I (or Bi–I bond), δ_s=74 cm^{-1} (or 90.2 cm^{-1}) and δ_{as}=54.3 cm^{-1} (or 71 cm^{-1}) from the symmetric and antisymmetric deformation vibration for SbI_3 (or BiI_3), respectively [14]. The absorption peaks of

Table 2 The experimental and calculated results for powder X-ray diffraction pattern of $Bi_3[SC(NH_2)_2]_3$. (Monoclinic: a=1.4009 nm, b=2.0170 nm, c=2.0397 nm, β=90.84°)

h, k, l	d_{exp}/nm	d_{cal}/nm	I/I_0	h, k, l	d_{exp}/nm	d_{cal}/nm	I/I_0
200	0.7008	0.7004	100	028	0.2472	0.2472	12
003	0.6794	0.6798	79	364	0.2395	0.2397	8
132	0.5199	0.5196	22	–601	0.2323	0.2323	19
014	0.4941	0.4943	74	621	0.2258	0.2257	15
300	0.4662	0.4669	6	–347	0.2232	0.2231	8
–223	0.4418	0.4418	15	–427	0.2202	0.2202	14
223	0.4371	0.4366	19	464	0.2182	0.2182	12
302	0.4215	0.4222	16	193	0.2104	0.2103	9
015	0.3998	0.3998	9	–642	0.2082	0.2080	15
044	0.3582	0.3585	24	094	0.2052	0.2052	7
–341	0.3386	0.3385	9	–376	0.1995	0.1996	13
402	0.3295	0.3297	24	393	0.1933	0.1933	17
062	0.3189	0.3193	46	259	0.1895	0.1895	7
235	0.3108	0.3106	57	–169	0.1865	0.1865	7
–325	0.2959	0.2958	58	439	0.1819	0.1819	6
–442	0.2778	0.2777	11	646	0.1787	0.1787	7
–316	0.2743	0.2742	8	568	0.1635	0.1636	6
–512	0.2688	0.2687	8	–658	0.1593	0.1593	6
–354	0.2630	0.2630	18	920	0.1539	0.1538	6
065	0.2595	0.2594	25	926	0.1395	0.1394	5
–363	0.2539	0.2539	18				

BiI_3 and SbI_3 can be found in the thiourea complexes. As Fig. 1. shows, there is a shoulder peak on the left side of the strong absorption at 151 cm^{-1} in the IR spectrum of the thiourea complex of SbI_3. The shoulder at 188 cm^{-1} may be from the symmetric stretching vibration (u_s=186.5 cm^{-1}) of the Sb–I bond. The absorption peak at 151 cm^{-1} is attributed to the overlap of the absorption peaks from the antisymmetric stretching vibration (u_{as}=147 cm^{-1}) of the Sb–I bond and that from the lattice vibration (u=173 cm^{-1}). As for the absorption peak at 59 cm^{-1}, it may be assigned to the antisymmetric deformation vibration (δ_{as}=54.3 cm^{-1}) of SbI_3. Similarly, in the infrared spectrum of the bismuth complex, the peak at 155 cm^{-1} is due to the overlap of the absorption peaks from the symmetric stretching vibration (u_s= 145.8 cm^{-1}) of the Bi–I bond and that from the lattice vibration (u=173 cm^{-1}) and the peak at 115 cm^{-1} is attributable to the overlap of the absorption peaks from the antisymmetric stretching vibration (u_{as}= 115.2 cm^{-1}) of BiI_3 and that from the lattice vibration (u=111 cm^{-1}). The absorption peak at 61 cm^{-1} is assigned to the antisymmetric deformation vibration (71 cm^{-1}) of BiI_3. From these assignments, it can be concluded that the antimony or bismuth ion both bonds directly to the iodine anion and is coordinated by the nitrogen atom in the thiourea complexes of antimony and bismuth triiodide.

The sulfur atom is not coordinated to the central metal ion in the complex may be explained by the effective ionic radius of metal ion and iodine anion. The effective ionic radius of the Sb^{3+}, Bi^{3+} and I^- is 0.76, 1.03 and 2.20 Å, respectively [16]. The effective ionic radius of the iodine anion is much larger than that of the antimony or bismuth ion. The covalent radius (1.03 Å) of the sulfur atom is also much larger than that (0.75 Å) of the nitrogen atom. When the smaller Sb^{3+} or Bi^{3+} ion is surrounded by three huge iodine anions, due to the steric hindrance, the thiourea molecule can only coordinate to the central metal ion through a donor atom with small ionic radius. This is why the nitrogen atom, not the sulfur atom coordinates to the antimony or bismuth ion in the complexes.

Table 3 gives the possible thermal decomposition reactions of the complexes. As Fig. 2A shows, there is an endothermic peak at 106.7°C in DTA curve of the thiourea complex of antimony triodide before the beginning of thermal decomposition. This may be attributable to the structure rearrangement in the coordination sphere of the complex. Because structure rearrangement does not lead to any mass loss, but needs certain energy. Then, a small en-

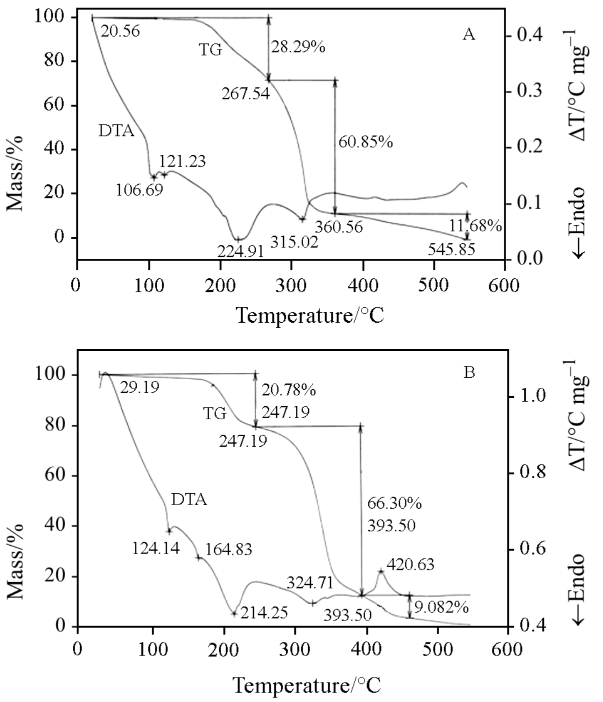

Fig. 2 TG and DTA curves of A – $SbI_3[SC(NH_2)_2]_3$ and B – $BiI_3[SC(NH_2)_2]_3$

dothermic peak in DTA curve appears at 121.3°C, again. Because there is not any corresponding mass loss of the sample in the TG curve, it can be attributable to another structure rearrangement or phase transformation in the solid complex. Another experiment also demonstrates, indeed, no mass loss of the sample of the Sb complex occurs below 125°C. After the sample of the Sb complex is heated at 125°C for 10 min, the relative content (16.6%) of Sb in the sample is very close to the theoretical content (16.67%) of Sb in the complex. Interestingly, it is found that the solid sample is softened at 125°C. Perhaps, this is an evidence for the phase transformation in the complex. Furthermore, as above mentioned, the sulfur atom of thiourea can not coordinate to the antimony or bismuth ion due to steric hindrance. However, heating a sample may overcome this steric hindrance effect. Therefore, when increasing temperature, the atom coordinating to the Sb ion may change from the nitrogen atom to the sulfur atom. This leads to the structure rearrangement in the coordination sphere of the complex. Of course, the phase transformation can also lead to an endothermic effect, but not a mass loss. However, it seems to be impossible that the phase transformations of the complex crystal can occur two times in such a small temperature range (100 to 120°C). Since there are three thiourea molecules in one complex molecule, the substitution of the sulfur atoms for the nitrogen atoms in the coordination sphere must carry out gradually with increasing temperature. This explains why there are two endothermic peaks in DTA curve. Perhaps the first endothermic peak at 106.7°C in DTA curve corresponds to the structure rearrangement in the coordination sphere and the second endothermic peak at 121.3°C corresponds to the phase transformation in the complex crystal. The first mass loss of the thiourea complex of SbI_3 happens at about 175°C corresponding to an endothermic peak in DTA curve. This is due to the loss of HI and $SC(NH_2)_2$ from the complex. The experimental mass loss (28.3%) is very close to the theoretical one (27.91%). The check experiment supports this conclusion. After the sample of the Sb complex is heated at 260°C for 10 min, the mass loss (26.8%) of the sample is close to the theoretical mass loss (27.91%) of the Sb complex. As Table 3 shows, the composition of the pyrolysis product in this step may be $SbI_2[S_2C_2N_4H_7]$. If this composition is reasonable, the theoretical content of Sb in $SbI_2[S_2C_2N_4H_7]$ will be 23.1%. The check experiment indicates that the relative content (21.8%) of Sb in the pyrolysis product determined by chemical method is close to the theoretical content of Sb in $SbI_2[S_2C_2N_4H_7]$. When temperature is over 267.5°C, all the ligands, iodine atoms and partial antimony atoms will be eliminated from the complex. The elimination reaction needs the energy and leads to the endothermic peak at 315°C in DTA curve. The experimental and theoretical mass losses are 60.85% and 60.42%, respectively. The check experiment demonstrates that the mass loss of the sample is 58.8% at 360°C and the relative content of Sb in the pyrolysis product is 98.9%. This shows that the pyrolysis product is the metal antimony. The residual antimony metal will be volatilized gradually with increasing temperature. Lastly, no residue can be found.

Figure 2B also shows two endothermic peaks at 124.1 and 164.8°C in DTA curve, before the beginning of thermal decomposition of the thiourea complex of bismuth triodide. Similarly, the endothermic peaks can also be attributed to the structure rearrangement in the coordination sphere of the complex or the possible phase transformation in the complex crystal. The check experiments confirm the conclusion. After the sample is heated at 150°C in a muffle furnace, no mass loss of the sample can be found and the relative content (25.3%) of Bi in the sample is very close to the percentage content (25.56%) of Bi in the complex. The first mass loss of the sample is mainly from elimination of the NH_3 and thiourea molecules and corresponds to the endothermic peak at 214.3°C in DTA curve. The experimental mass loss (20.78%) consists very well with the theoretical one (20.69%). The check experiment shows, if the sample is heated at 245°C for 10 min, the mass loss of the sample will be 23.3%. This is slightly larger than the theoretical

Table 3 Thermal dccomposition data of $SbI_3[SC(NH_2)_2]_3$ and $BiI_3[SC(NH_2)_2]_3$

Reaction	DTA/°C	Mass loss/%	
		W_{exp}	W_{theor}
$SbI_3[SC(NH_2)_2]_3$			
↓ structural rearrangement	106.7 (endo)		
↓	(125°C)	0.0[*]	
↓	[Sb]	16.56%[**]	16.67%[**]
$SbI_3[SC(NH_2)_2]_3$			
↓ structural rearrangement	121.2 (endo)		
$SbI_3[SC(NH_2)_2]_3$			
↓ –HI, $–SC(NH_2)_2$	224.9 (endo)	28.89	27.91
↓	(250°C)	26.8[*]	
↓	[Sb]	21.8%[**]	23.1%[**]
$SbI_2[SC(NH_2)_2]NHSCNH_2$			
↓ $–I_2$, $–SC(NH_2)_2$	315.0 (endo)	60.85	60.42
↓ $–SCNH_2NH$, –0.3Sb			
↓	(360°C)	58.8[*]	
↓	[Sb]	98.9%[**]	100%[**]
0.7Sb			
↓ –0.7Sb		11.68	11.67
$BiI_3[SC(NH_2)_2]_3$			
↓ structural rearrangement	124.1 (endo)		
↓	(150°C)	0.0[*]	
↓	[Bi]	25.3%[**]	25.56%[**]
$BiI_3[SC(NH_2)_2]_3$			
↓ structural rearrangement	164.8 (endo)		
$BiI_3[SC(NH_2)_2]_3$			
↓ $–2SC(NH_2)_2$, $–NH_3$	214.3 (endo)	20.78	20.69
↓	(245°C)	23.3[*]	
↓	[Bi]	33.4%[**]	32.2%[**]
$BiI_3(HNCS)$			
↓ –HNCS, $–1.5I_2$	324.7 (endo)	66.30	66.53
↓ –0.5Bi			
↓	(390°C)	68.7[*]	
↓	[Bi]	99.3%[**]	100%[**]
0.5Bi			
↓ –0.37Bi	420.6 (exo)	9.06	9.07
↓ +0.195O			
$0.065Bi_2O_3$		3.86	3.70

[*] The percentage mass loss of the sample measured in the check experiment, [**] the relative content of Sb or Bi in the intermediate measured in the check experiments

loss (20.69). In this case, the composition of the pyrolysis product may be $BiI_3(HNCS)$, hence, the percentage content of Bi in the product will be 32.2%. As Table 3 shows, the relative content of Bi in the pyrolysis product determined by chemical method is 33.4%. This demonstrates that the composition of the product in the above pyrolysis reaction may be correct. Then, there is a larger mass loss in TG curve. The sample will lose HNCS, iodine and partial bismuth atoms. The break of the Bi–I bond in the complex and the volatilization of the HNCS, iodine and bismuth atoms from the sample need a certain energy, hence, this corresponds to an endothermic peak at 324.7°C. The check experiment confirms that the mass loss (68.7%) of the sample in this step is close to the theoretical mass loss (66.53%) and the relative content of Bi in the product is 99.3%. This indicates that the pyrolysis product must be metal Bi. We have also noted that the product displays metal luster. Over 400°C, the residual bismuth can be oxidized by oxygen in air. The oxidation reaction leads to an exothermic effect, so, there is an exothermic peak in DTA curve. The partial Bi_2O_3 will volatilize gradually with increasing temperature. Last, the thermal decomposition product is a yellow residue (Bi_2O_3).

Conclusions

The new solid thiourea complexes of antimony and bismuth can be synthesized through a direct solid reaction between antimony or bismuth triiodide and thiourea powders. The formula of the complex is $SbI_3[SC(NH_2)_2]_3$ or $BiI_3[SC(NH_2)_2]_3$. The crystal structure of the two complexes belongs to monoclinic system. The far-infrared spectra of the complexes reveal that there is no Sb–S or Bi–S bond in the complexes and the Sb or the Bi ion are not only bonded directly to the iodine anion, but also coordinated to the nitrogen atom of thiourea. The thermal analysis indicates that there may be structure rearrangement in the coordination sphere and phase transformation in the range from 100 to 120°C for $SbI_3[SC(NH_2)_2]_3$ and in the range from 120 to 160°C for $BiI_3[SC(NH_2)_2]_3$, respectively. The check experiments confirm the thermal decomposition process of the Sb and the Bi complex and the occurrence of structure rearrangement or phase transformation.

References

1 H. Oki and K. Otsuka, Bull. Chem. Soc. Jpn., 49 (1976) 1841.
2 R. A. Siddiqui, P. Raj, A. K. Saxena and S. K. Dixit, Synth. Reac. Inorg. Met.-org. Chem., 26 (1996) 1189.
3 G. R. Willey, L. T. Daly, P. P. Meehan and M. G. B. Drew, J. Chem. Soc. Dalton Trans., (1996) 4045.
4 M. S. Singh and K. P. Rao, Synth. Reac. Inorg. Met.-org. Chem., 29 (1999) 541.
5 G. Cantos, C. L. Barbieri, M. Iacomini, P. A. J. Gorin and L. R. Travassos, Biochem. J., 289 (1993) 155.
6 J. Kaloustian, A. M. Pauli, G. Pieroni and H. Portugal, J. Therm. Anal. Cal., 70 (2002) 963.
7 L. Xi, L. Yi, W. Jun, L. Huigang and Q. Songsheng, J. Therm. Anal. Cal., 67 (2002) 589.
8 N. N. Greenwood and A. Earnshaw, Chemistry of the Elements (2nd Ed.), Reed Educational and Professional Publishing Ltd. (1997) p. 553.
9 Y. C. Guo, S. R. Luan, Y. R. Chen, X. S. Zang, Y. Q. Jia, G. Q. Zhong and S. K. Ruan, J. Therm. Anal. Cal., 68 (2002) 1025.
10 R. R. Jia, Y. X. Yang, Y. R. Chen and Y. Q. Jia, J. Therm. Anal. Cal., 76 (2004) 157.
11 A. Yamaguchi, R. P. Penland, S. Mizushima, T. J. Lane, C. Curran and J. V. Quagliano, J. Am. Chem. Soc., 80 (1958) 527.
12 R. Rivest, Can. J. Chem., 40 (1962) 2234.
13 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley & Sons Inc., 1978 (3rd Ed.).
14 D. M. Adams and J. B. Cornell, J. Chem. Soc.(A), (1967) 884.
15 R. D. Shannon, Acta Crystallogr., Sect. A.: 32 (1976) 751.

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