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SOLID PHASE SYNTHESIS, CHARACTERIZATION OF HEXAMETHYLENETETRAMINE COMPLEXES OF ANTIMONY AND BISMUTH TRICHLORIDE

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Abstract

New hexamethylenetetramine complexes of antimony and bismuth trichloride were synthesized through a solid phase reaction of hexamethylenetetramine and antimony or bismuth trichloride. The formula of the complex is $MCl_3(C_6H_{12}N_4)_2\cdot H_2O$ (M=Sb, Bi). The crystal structure of the complexes belongs to monoclinic system and the lattice parameters: a=1.249 nm, b=1.4583 nm, c=1.6780 nm and β=91.78° for $SbCl_3(C_6H_{12}N_4)_2\cdot H_2O$ and a=1.3250 nm, b=1.3889 nm, c=1.7449 nm and β=98.94° for $BiCl_3(C_6H_{12}N_4)_2\cdot H_2O$. Far-infrared spectra reveal that the antimony or bismuth ion is coordinated by the nitrogen atom of the hexamethylenetetramine. The thermal analysis also demonstrates the complex formation between the antimony or bismuth ion and hexamethylenetetramine. The intermediate and final residues in the thermal decomposition process have been analyzed to check the pyrolysis reaction.

Keywords: crystal structure, far-infrared spectra, hexamethylenetetramine complex of Sb and Bi, solid phase synthesis, thermal decomposition

Introduction

A lot of solid complexes of the transition metal ions and various ligands were synthesized and studied. By comparison, the number of the solid complexes of the main group metal ion, such as antimony and bismuth ion, is less [1–3], because many inorganic salts of the antimony and bismuth are very easily hydrolysed in the aqueous solution [4], hence, to synthesize the solid complexes of antimony or bismuth ion and organic ligands through a liquid phase reaction in the aqueous solution is very difficult. The solid phase reaction is

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a simple synthesis method and has widely been used to the synthesis of the inorganic materials at high temperature. However, the complexes of the transition metal ions and some organic ligands can be synthesized by the solid phase reaction at room temperature [5]. Perhaps, the solid complexes of the antimony or bismuth ion and organic ligands can also be prepared by a solid phase reaction.

Some complexes of the antimony and bismuth can possess a certain biologic or medicinal function [6–8]. The complexes of the antimony and bismuth can also treat the cancer [9, 10]. Therefore, to synthesize the new complexes of the antimony or bismuth ion and various organic ligands is very interesting not only for the main group elements chemistry, but also for the bioinorganic and pharmaceutical chemistry. Hexamethylenetetramine can be used to medicine and the hexamethylenetetramine complex of some transition metal ions, such as cobalt and nickel ion, were reported and thermal decomposition of the complexes was also studied [11–13]. In this paper, we shall give the solid phase synthesis process of new solid complexes of antimony and bismuth ion with hexamethylenetetramine, the results of indexing to the powder X-ray diffraction patterns of the complexes and the far-infrared spectra of the complexes. Especially, we shall report the thermal decomposition of the complexes and give some analytical results for the intermediate and final residues in the thermal decomposition process to check the pyrolysis reaction of the complexes.

Experimental

All the chemicals used in the experiments are analytical reagent. First, to weigh 1.141 g (5 mmol) $SbCl_3$ and 1.402 g (10 mmol) $[(CH_2)_6N_4]_2$ and very well to mix up two reactants together. The molar ratio of $SbCl_3$ to $[(CH_2)_6N_4]_2$ is 1:2. Then, to drop a few amount of acetonitrile to the mixture and carefully to grind the mixture in an agate mortar. The reaction conducts in grinding at room temperature for about 10 h. At the first, the mixture becomes slightly viscous, then, gradually becomes the white loose powder. This indicates that the reaction does happen. The reactant mixture holds at 50°C for 14 h. The resultant is washed repeatedly by the acetonitrile until no antimony ion in the washing solution can be detected. Last, the resultant is dried in a vacuum drying oven. The resultant is powdery and does not show appreciable moisture in air. The resultant of the solid phase reaction of $BiCl_3$ and $[CH_2)_6N_4]_2$ can also be obtained by same process.

Carbon, hydrogen and nitrogen in the resultants were analyzed by an Elementar Vario EL elemental analysis. The chlorine ion in the resultant was measured by the chlorine ion selective electrode. Antimony was analyzed by the iodimetry and bismuth by EDTA and the standard zinc chloride solution back titration. The results are shown in Table 1. The powder X-ray diffraction patterns of the resultants were recorded by a D/max-YB X-ray diffractometer, $CuK_{\alpha 1}$ radiation; Ni filter; scanning rate $2(2\theta)\ min^{-1}$; at room temperature. The results of indexing to the X-ray diffraction pattern are listed in Table 2. The far-infrared spectra of the resultants were measured by a Nicolet 5D-FT spectrometer and the cesium iodide disk technique. The far-infrared spectra of the resultants are shown in Fig. 1. The thermal decomposition process of the resultants were studied by a LCT-1 differential thermal balance in air, with a heating rate of 10°C min^{-1} and the reference was α-Al_2O_3. The thermogravimetric and differential thermal analysis curves are shown in Fig. 2 and the possible pyrolysis reactions, experimental and calculated results for the resultants are summarized in Table 3. To check the pyrolysis process, a certain amount (about 400 mg) of the complex is placed in an alumina crucible and heated in a muffle furnace at a certain temperature for about 10 to 20 min. Then, to measure the mass loss of the sample before and after heating and to take a certain amount (about 50 mg) of the pyrolysis product and to determine the content of Sb or Bi in the pyrolysis product. Then, to continue heating the residual sample in the alumina crucible and to repeat the above mentioned procedure until the final residue is gotten. The results are listed in Table 4.

Table 1 The elemental analysis for the resultants

Resultant		C	H	N	M	Cl
$SbCl_3(C_6H_{12}N_4)_2 \cdot H_2O$	calculated/%	27.37	4.99	21.29	23.12	20.2
	found/%	27.93	5.13	21.79	22.85	19.5
$BiCl_3(C_6H_{12}N_4)_2 \cdot H_2O$	calculated/%	23.46	4.24	18.25	34.04	17.4
	found/%	23.47	4.27	18.44	33.94	16.9

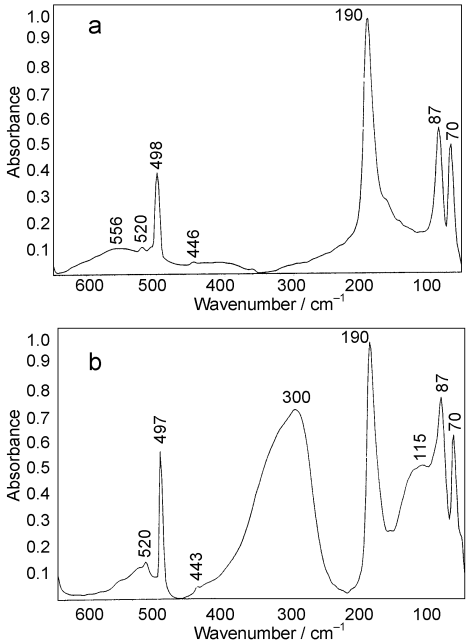

Fig. 1 The infrared spectra of a – $SbCl_3(C_6H_{12}N_4)_2 \cdot H_2O$ and b – $BiCl_3(C_6H_{12}N_4)_2 \cdot H_2O$

Table 2 The experimental data and the calculated results for powder X-ray diffraction pattern of $SbCl_3(C_6H_{12}N_4)_2 \cdot H_2O$ and $BiCl_3(C_6H_{12}N_4)_2 \cdot H_2O$

$SbCl_3(C_6H_{12}N_4)_2 \cdot H_2O$, monoclinic system a=1.2490 nm, b=1.4583 nm, c=1.6870 nm β=91.78°				$BiCl_3(C_6H_{12}N_4)_2 \cdot H_2O$, monoclinic system a=1.3250 nm, b=1.3889 nm, c=1.7449 nm β=98.94°			
h,k,l	d_{exp}/nm	d_{calc}/nm	I/I_0	*h,k,l*	d_{exp}/nm	d_{calc}/nm	I/I_0
1 1 1	0.8185	0.8184	6	0 0 1	1.3886	1.3889	20
–1 0 2	0.7087	0.7090	6	0 1 2	0.7333	0.7323	57
1 2 1	0.5863	0.5868	50	2 0 1	0.5824	0.5825	43
1 2 2	0.5001	0.5007	12	–2 1 3	0.4449	0.4447	86
0 2 3	0.4467	0.4452	100	2 1 3	0.3860	0.3861	34
3 1 1	0.3874	0.3868	43	3 0 2	0.3672	0.3670	22
–1 3 3	0.3548	0.3547	8	0 0 5	0.3432	0.3447	100
–1 4 3	0.2982	0.2983	16	0 4 3	0.2974	0.2972	13
2 0 5	0.2927	0.2929	9	–4 1 4	0.2769	0.2769	46
–2 2 5	0.2778	0.2779	45	0 5 1	0.2746	0.2742	91
3 0 5	0.2577	0.2581	7	4 0 3	0.2671	0.2671	95
–5 0 1	0.2479	0.2481	16	5 1 0	0.2573	0.2573	14
3 4 3	0.2446	0.2445	8	–5 2 1	0.2474	0.2476	13
–3 4 5	0.2149	0.2149	5	–5 2 0	0.2449	0.2450	17
0 7 0	0.2084	0.2083	6	3 4 4	0.2202	0.2204	25
–5 4 3	0.1951	0.1950	8	–6 0 4	0.2081	0.2081	5
3 5 5	0.1933	0.1933	8	–4 0 8	0.1944	0.1944	38
–2 6 5	0.1889	0.1890	12	3 4 6	0.1886	0.1885	12
–3 7 3	0.1776	0.1776	6	–5 2 7	0.1880	0.1870	12
–2 8 1	0.1743	0.1742	7	–6 4 3	0.1830	0.1830	22
–4 4 9	0.1487	0.1487	5	0 8 0	0.1737	0.1736	6
–6 5 6	0.1468	0.1467	5	0 7 5	0.1719	0.1720	9
3 6 9	0.1386	0.1387	3	–1 4 9	0.1692	0.1693	28
–5 6 9	0.1290	0.1290	3	–5 1 9	0.1663	0.1663	20
7 8 3	0.1238	0.1237	3	–4 7 5	0.1572	0.1573	30
				3 5 8	0.1524	0.1524	11
				5 8 3	0.1375	0.1375	11
				–6 8 3	0.1351	0.1352	4
				–4 9 6	0.1289	0.1289	5
				–6 7 8	0.1276	0.1277	7
				–6 9 1	0.1264	0.1265	12
				6 9 2	0.1230	0.1231	11

Table 3 Thermal decomposition data of $SbCl_3(C_6H_{12}N_4)_2{\cdot}H_2O$ and $BiCl_3(C_6H_{12}N_4)_2{\cdot}H_2O$

Reaction	T/°C	Mass loss/%	
		found	calc.
$SbCl_3(C_6H_{12}N_4)_2{\cdot}H_2O$ $\downarrow -H_2O$	202 (endo)	3.2	3.4
$SbCl_3(C_6H_{12}N_4)_2$ $\downarrow -3N_2H_4$	208 (exo)	18.1	18.3
$SbCl_3C_{12}H_{12}N_2$ $\downarrow -(N_2, C_8H_8, 0.5Cl_2)$	269 (endo)	32.0	31.8
$SbCl_2C_4H_4$ $\downarrow -2/3SbCl_3$ $\downarrow -C_4H_4$	481 (exo) 532 (exo)	40.3	38.8
1/3Sb	561	6.4*	7.7
$BiCl_3(C_6H_{12}N_4)_2{\cdot}H_2O$ $\downarrow -H_2O$	207 (endo)	3.0	3.0
$BiCl_3(C_6H_{12}N)_2$ $\downarrow -3N_2H_4$	216 (exo)	16.0	15.7
$BiCl_3C_{12}H_{12}N_4{\cdot}H_2O$ $\downarrow -1.5Cl_2$	263 (endo)	16.8	17.3
$BiC_{12}H_{12}N_2$ $\downarrow -N_2C_4H_4$ $\downarrow -C_8H_8$	381 (exo) 532 (exo)	32.1	30.0
Bi	558	32.1*	34.0**

*Percentage mass of the residue in the sample
**Percentage content of Bi in the complex

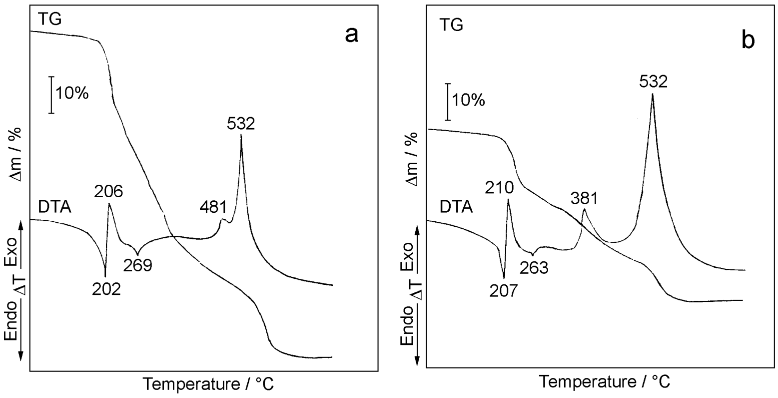

Fig. 2 TG and DTA curves of a – $SbCl_3(C_6H_{12}N_4)_2{\cdot}H_2O$ and b – $BiCl_3(C_6H_{12}N_4)_2{\cdot}H_2O$

Results and discussion

From the results of elemental analysis for the resultants, the compositions of two resultants are $SbCl_3C_{12}H_{26}N_8O$ and $BiCl_3C_{12}H_{26}N_8O$, respectively. Therefore, the corresponding formula will be $SbCl_3(C_6H_{12}N_4)_2 \cdot H_2O$ and $BiCl_3(C_6H_{12}N_4)_2 \cdot H_2O$.

All the diffraction peaks in each pattern can be readily indexed by a set of lattice parameters according to monoclinic system. As Table 2 shows, the largest relative deviation between the calculated and experimental spacing is less than 0.4%. This indicates that the resultants are single phase compounds with a monoclinic symmetry. The crystal structure of the antimony and bismuth trichloride belongs to orthorhombic system (JCPDS1-248 and 24-1003) and of the hexamethylenetetramine belongs to cubic system (JCPDS3-0135). The crystal structure of the resultants belongs neither to cubic nor to orthorhombic system, but to monoclinic system. Obviously, the resultant must be new hexamethylenetetramine complex of antimony or bismuth trichloride.

As Fig. 1 shows, there are two strong absorption peaks at 498 cm^{-1} (or 497 cm^{-1}) and 190 cm^{-1} in the far-infrared spectra of complexes. The frequency of the stretching vibration of the Pd–N or Pt–N bond is about 500 cm^{-1} [14]. The absorption peak at 498 or 497 cm^{-1} may be assigned to the stretching vibration of the Sb–N or Bi–N bond and that at 190 cm^{-1} to the deformation of the N–Sb–N or N–Bi–N bond in the complex. In the infrared spectrum of the complex of bismuth, there are two very strong absorption peaks at 300 and 115 cm^{-1}. The frequency of the symmetric stretching vibration of the Bi–Cl bond and the deformation vibration of the Cl–Bi–Cl bond in a gaseous $BiCl_3$ molecule is 342 and 123 cm^{-1}, respectively [14]. In the complex of the bismuth trichloride and hexamethylenetetramine, the vibration frequency of the above bonds becomes lower due to the formation of the coordination bond between the bismuth ion and ligand or the steric hindrance caused by two large hexamethylenetetramine molecules. The absorption peaks at 300 and 115 cm^{-1} may be from the symmetric stretching vibration of the Bi–Cl bond and deformation vibration of the Cl–Bi–Cl bond in the complex, respectively. The frequency of the symmetric stretching vibration of the Sb–Cl bond and deformation vibration of the Cl–Sb–Cl bond in a gaseous $SbCl_3$ molecule is 381 and 151 cm^{-1}, respectively [14]. The corresponding absorption peaks do not appear in the infrared spectrum of the complex of the antimony trichloride. This means the absence of the Sb–Cl bond in the complex. Why is the Sb ion not coordinated by the chlorine anion in the complex? This is mainly because the effective ionic radius (0.076 nm) of the Sb^{3+} ion is much less than that (0.103 nm) of the Bi^{3+} ion [15]. When a smaller Sb ion is coordinated by two large hexamethylenetetramine molecules, the larger chlorine anion (0.181 nm) can not close to the Sb ion and be only in the outer coordination sphere of the complex. There is a weaker absorption peak at 446 or 443 cm^{-1} in the infrared spectrum of the antimony or bismuth complex. This peak is from the stretching vibration of the Sb–O or Bi–O bond. The oxygen atom of the water can also coordinate to the Sb or Bi ion. The frequency of the stretching vibration of a chemical bond relates to the mass of the atom in the bond. The heavier the bonding atom is, the lower the vibration frequency of the bond is. The oxygen atom is slightly heavier than the nitrogen atom and much lighter than the chlorine atom. The stretching vibration frequency (443 cm^{-1}) of the Bi–O bond must be slightly lower than that (497 cm^{-1}) of the Bi–N bond and much higher than that (300 cm^{-1}) of the Bi–Cl bond. Similarly, the absorption peak at 446 cm^{-1} in the infrared spectrum of the complex of antimony may be from the stretching vibration of the Sb–O bond. The absorption peaks at 556 (or 560) and 520 cm^{-1} may be from the vibrations of the bonds in the ligand. The absorption peaks in a low frequency region (<100 cm^{-1}), such as at 87 or 70 cm^{-1}, are generally from the lattice vibration of the solid compound.

There is a similar endothermic peak at about 200°C in DTA curves of the complexes. The percentage mass loss shows that the complexes contain the same number of water molecules. This consists with the elemental analysis. Such high temperature of the dehydration can demonstrate that the oxygen atom of the water molecules must be coordinated directly to the Sb or Bi ion. This also supports the assignment for the absorption peaks at 446 and 443 cm^{-1} from the stretching vibration of the Sb–O or Bi–O bond. The second mass loss of the complexes occurs at about 210°C. The qualitative test shows that the pyrolysis product is basic gas and can let the wet pH paper become blue. This may be the loss of three N_2H_4 molecules from the hexamethylenetetramine. Perhaps, the combustion of N_2H_4 leads to the exothermic peak in DTA curve. There are eight nitrogen atoms in two hexamethylenetetramine molecules. The fact that only six, not eight, nitrogen atoms are eliminated from the complex in this pyrolysis step may mean that the chemical environment of the two nitrogen atoms are different from that of the eliminated six nitrogen atoms. Maybe, it is just through the two nitrogen atoms that the hexamethylenetetramine molecules are coordinated directly to the metal ion. This is consistent with the presence of the absorption peak from the vibration of the Sb–N or Bi–N and N–Sb–N or N–Bi–N bonds in the infrared spectra of the complexes. The chlorine anions may enter from the outer coordination sphere to the inner coordination sphere of the complex and bond directly to the Sb ion when the absence of the steric hindrance caused by large hexamethylenetetramine molecules after the partial decomposition of the ligands. The experimental percentage mass loss (32.0%) of the complex of antimony in the third pyrolysis step is much larger than that (16.8%) of bismuth. This means that two complexes have different coordination structure. The qualitative test reveals that the pyrolysis product of two complexes in this step shows acidity and can let the wet pH paper become red. This may be due to the elimination of the chlorine from the complex. The final residue of the samples at above 550°C possesses metallic luster and the analysis results can demonstrate that the residue does be metallic Sb or Bi. However, the mass of the residue of the metallic Sb is much less than the theoretical content of Sb in the complex. This may be because some Sb lost as $SbCl_3$ at about 480–530°C due to the volatilization of the $SbCl_3$ molecule [4]. As Table 4 shows, the percentage mass loss of the sample at each pyrolysis step in the test experiment can consist generally with that in the thermal analysis of the complexes. The metal contents in the intermediates after each pyrolysis step can also demonstrate that the pyrolysis reactions in Table 3 are reliable. Perhaps, the error of determination for the metal content in the pyrolysis residue is larger because the amount of the residue used in chemical analysis is too small. The final pyrolysis residue of the complex of antimony or bismuth in the test experiment is not pure metallic Sb or Bi. This may be mainly because the equipment and experimental condition in the test experiment is very different from that in the thermal analysis.

Table 4 The mass loss of the samples and the Sb or Bi content in the intermediates after the pyrolysis reaction of $SbCl_3(C_6H_{12}N_4)_2{\cdot}H_2O$ and $BiCl_3(C_6H_{12}N_4)_2{\cdot}H_2O$ at different temperautre

Reaction and intermediate	*T*/°C	Mass loss/%		Metal content/%	
		found	calc.	found	calc.
$SbCl_3(C_6H_{12}N_4)_2{\cdot}H_2O$					
↓	180	3.3	3.4		
$SbCl_3(C_6H_{12}N_4)_2$					
↓	200	19.2	18.3		
$SbCl_3C_{12}H_{12}N_2$				29.7	29.5
↓	260	37.8	31.8		
$SbCl_2C_4H_4$				52.9	49.7
↓					
residue	560	8.4*	7.7	91.0	100
$BiCl_3(C_6H_{12}N_4)_2{\cdot}H_2O$					
↓	180	2.9	3.0		
$BiCl_3(C_6H_{12}N_4)_2$					
↓	210	19.6	15.7		
$BiCl_3C_{12}H_{12}N_2$				43.5	41.8
↓					
residue	560	36.3*	34.0**	90.8	100

*Percentage mass of the residue in the sample

**Percentage content of Bi in the complex

Conclusions

New hexamethylenetetramine complex of antimony or bismuth trichloride can be synthesized through a solid phase reaction of hexamethylenetetramine and antimony or bismuth trichloride. The formula of the complex is $SbCl_3(C_6H_{12}N_4)_2{\cdot}H_2O$ and $BiCl_3(C_6H_{12}N_4)_2{\cdot}H_2O$. The crystal structure of the complexes belongs to monoclinic system. The infrared spectra show that there are the Sb–N or Bi–N and Sb–O or Bi–O bonds in the complexes. The chlorine anions are coordinated directly to the Bi ion in the bismuth complex, but not coordinated to the Sb ion and are in the outer coordination sphere of the antimony complex. The hexamethylenetetramine molecule may coordinate to the Sb or Bi ion by one nitrogen atom. The oxygen atom of the water is also coordinated directly to the metal ion. The thermal analysis demonstrates the complex formation between the Sb or Bi ion and hexamethylenetetramine. The mass loss of the sample and determination of the metal content in the intermediate in test experiment can support the pyrolysis reactions in the thermal analysis of the complexes.

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