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Solid Phase Synthesis and Characterization of Antimony(III) Ternary Complexes Containing Phthalate

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ABSTRACT

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Received: 29 December 2016 Accepted: 13 January 2017 Published: 24 February 2017 The complexes of antimony(III) with phthalic acid (H₂phth) and a ternary complex using imidazole as secondary ligand were synthesized by solid-solid reaction at room temperature. The complexes were characterized by chemical and elemental analyses, infrared spectra, X-ray powder diffraction and thermogravimetric analysis. The compositions of the complexes were [Sb(Hphth)₂Cl]·2H₂O and [Sb(Hphth)(Im)Cl₂]·H₂O (Im = imidazole), respectively. The antimony(III) ions were all hexa-coordinated by the carboxyl oxygen atoms from the Hphth⁻ ligands and chlorine atom for [Sb(Hphth)₂Cl]·2H₂O and by the carboxyl oxygen atoms from the Hphth⁻ ligand and nitrogen atom from imidazole and chlorine atoms for [Sb(Hphth)(Im)Cl₂]·H₂O. The thermal decomposition processes of the complexes under nitrogen atmosphere included dehydration and pyrolysis of the ligands and the final residue was antimonous oxide.

KEYWORDS

Antimony(III), Ternary complex, Phthalic acid, Solid-solid reaction, Thermal decomposition.

INTRODUCTION

Main group elements do not easily form complexes with organic ligands because of the special properties, but the complexes of main group metal ions, such as antimony ion, can possess a certain biological functions. The fifth main group metal compounds including inorganic and metal-organic complexes have been studied for decades due to the interesting medical, physical properties and material functions [1,2]. The complexes of antimony have biological functions, such as sterilization, antibacterial activity, anticancer and so forth. Antimony 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 [3]. Many of antimony(III) complexes have been clinically used because of their biological activities and drug efficacies [4-8]. In recent years, the application of antimony complexes in cancer chemotherapy has become a topic of interest and antimony(III) compounds have been tested in vitro for their cytotoxic effects on the proliferation of some leukemia and solid tumor cells [9-13]. The research of antimony interactions with potential targeting

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biomolecules, including peptides, proteins and enzymes, will bring about an understanding of the mechanism of action of antimony-containing complexes and in turn to the further application of antimony in medicine. Imidazole is a chemical that is widely used in the fields of biology and medicine and is usually a unidentate ligand and forms complexes with metal ions through its nitrogen atom. The complexes of imidazole and its derivatives have good biological activities [14,15]. We have a great interest in the coordination chemistry of antimony and demonstrate that polycarboxylic frameworks are able to accommodate antimony [16-19]. Because the inorganic salts of antimony are easily hydrolyzed in the aqueous solution, so the aqueous solution reaction preparation for some complexes of antimony is very difficult [20]. In this paper, we report the syntheses and characterization of the two antimony(III) complexes of phthalic acid as well as imidazole as secondary ligand by means of solid-solid reaction at room temperature.

EXPERIMENTAL

All chemicals used in the experiments were analytical reagents as received from commercial sources and without further purification. Phthalic acid (H₂phth), lithium hydroxide (LiOH·H₂O), antimony trichloride and imidazole were received from Chengdu Kelong Chemical Reagent Company, China.

The carbon, hydrogen, nitrogen, chloride and oxygen in the complexes were determined by Vario EL CUBE elemental analyzer for Germany Elemental Analysis System Company. The antimony in the complexes was determined by iodometric method. 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_{a1} radiation ($\lambda = 0.154056$ nm), Ni filter, scanning rate was 8° (20) min⁻¹ at room temperature. Infrared spectra of the complexes were measured by a Nicolet 5700 Fourier transform infrared spectrometer from America using potassium bromide pellets in the region of 4000-400 cm⁻¹. 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⁻¹.

Synthesis of lithium hydrogen phthalate: Phthalic acid (10 mmol, 1.66 g) and lithium hydroxide (10 mmol, 0.42 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. Finally, the white powder of lithium hydrogen phthalate (LiHphth) was obtained.

Synthesis of complex [Sb(Hphth)₂Cl]·2H₂O: 2 mmol (0.46 g) of antimony trichloride and 4 mmol (0.69 g) of lithium hydrogen phthalate were placed in an agate mortar and the mixture was continuously ground at room temperature about 4 h. Finally, the resulting product was washed with anhydrous

methanol and acetone and filtered by vacuum and dried in a vacuum drying oven at 40 °C for 24 h. A white powder was obtained and the yield was 81 %.

Synthesis of complex [Sb(Hphth)(Im)Cl₂]·H₂O: 2 mmol (0.46 g) antimony trichloride and 2 mmol (0.34 g) lithium hydrogen phthalate were placed in an agate mortar and the mixture was ground to dry powder. Afterwards 2 mmol (0.14 g) of imidazole was added to the above mixture and was continuously ground at room temperature about 4 h. Finally, the product was washed with anhydrous methanol and acetone and filtered by vacuum and dried in a vacuum drying oven at 40 °C for 24 h. A white powder was obtained and the yield was 86 %.

RESULTS AND DISCUSSION

Composition of antimony complexes: The elemental analyses results of the complexes are listed in Table-1. The composition formulae of the complexes are $SbC_{16}H_{14}O_{10}Cl$ ($M_r = 523.50$) and $SbC_{11}H_{11}O_5N_2Cl_2$ ($M_r = 443.88$), respectively. The calculated results of mass fraction of each element in the complexes are very close to the experimental ones. The molecular formulae of the complexes is [Sb(Hphth)_2Cl]·2H_2O and [Sb(Hphth)(Im)Cl_2]·H_2O, respectively.

X-ray powder diffraction analysis: Figs. 1 and 2 depicted the XRD patterns of complexes [Sb(Hphth)₂Cl]·2H₂O and [Sb(Hphth)(Im)Cl₂]·H₂O. It is seen that complexes [Sb(Hphth)₂Cl] ·2H₂O at $2\theta = 5.41^{\circ}$, 40.66° and 15.82° and [Sb(Hphth)(Im) Cl₂]·H₂O at $2\theta = 9.84^{\circ}$, 28.44° and 27.42°, respectively, produce the three strong peaks, while the three strong peaks of the reactants of SbCl₃ (JCPDS card no. 01-0248) at $2\theta = 8.13^{\circ}$, 18.55° and 23.93° and phthalic acid (JCPDS card no. 13-0823) at $2\theta = 15.45^{\circ}$, 27.08° and 22.32° and imidazole (JCPDS 15-0978) at $2\theta = 20.80^{\circ}$, 20.42° and 25.90° disappear in the complexes. The diffraction angle (2 θ), spacing (d) and diffractive intensity



TABLE-1									
ELEMENTAL ANALYSES RESULTS OF ANTIMONY COMPLEXES (CALCULATED VALUES ARE IN BRACKETS)									
Complex	Formula	Sb (%)	C (%)	H (%)	N (%)	Cl (%)	O (%)		
[Sb(Hphth)2Cl]·2H2O	$C_{16}H_{14}O_{10}ClSb$	22.93 (23.26)	36.49 (36.71)	2.51 (2.70)	-	6.49 (6.77)	30.32 (30.56)		
[Sb(Hphth)(Im)Cl ₂]·H ₂ O	$C_{11}H_{11}O_5N_2Cl_2Sb$	27.58 (27.43)	29.37 (29.77)	2.11 (2.50)	6.29 (6.31)	16.24 (15.97)	18.41 (18.02)		





Infrared spectra: IR spectra of the complexes are shown in Figs. 3 and 4. The absorption peaks present in infrared spectrum of the complex $[Sb(Hphth)_2Cl]\cdot 2H_2O$ were much less than that of potassium hydrogen phthalate, indicating that the symmetry of the complex was higher than that of the ligand. IR spectra of the two complexes show that the broad strong absorption band at 3445 cm⁻¹ or 3425 cm⁻¹ is due to the v(O-H) of water molecules. The stretching vibration peaks of $v_{as}(COO^{-})$ and $v_{s}(COO^{-})$ are observed at 1688 cm⁻¹ and 1406 cm⁻¹ for free phthalic acid ligand. In Fig. 3, the absorption band at 1635 cm⁻¹ is assigned to the asymmetric stretching vibration of carboxylic groups, while the absorption band at 1378 cm⁻¹ corresponds to the symmetric stretching vibration of carboxylic groups. Usually, the difference value (Δv) between $v_{as}(COO^{-})$ and $v_{a}(COO^{-})$ in the IR spectra can be used to derive infor-mation regarding the bonding modes of carboxylic anions. Namely, the Δv of 257 cm⁻¹ indicates that the carboxylic groups in the complex [Sb(Hphth)2Cl]·2H2O exhibit monodentate or bridge coordination mode [16]. The bands at 589 and 474 cm⁻¹ are assigned to the stretching vibration peaks of the Sb-O bonds, which are formed the water-O and carboxylate-O atoms, respectively. Therefore, it is concluded that phthalate behaves as bidentate mode and binds to the antimony ion through the oxygen atom in water molecule and carboxylate oxygen atoms in the deprotonated carboxyl groups [21]. In Fig. 4, the absorption band at 3144 cm⁻¹ is due to the $\nu(N-H)$ of imidazole. The infrared spectrum of [Sb(Hphth)(Im)Cl₂]·H₂O exhibits salient features at 1581 and 1387 cm⁻¹, which are assigned to the $v_{as}(COO^{-})$, v(C=N) and $v_s(COO^-)$ stretching vibration peaks of the azomethine and coordinated carboxyl groups $(\Delta v [v_{as}(COO^{-}) - v_{s}(COO^{-})] = 194$ cm⁻¹). It indicates that the oxygen atoms of the carboxyl in the complex is directly linked with the antimony ion and the presence of carboxylate groups coordinate to antimony ion in bidentate chelate coordination mode [22,23]. The stretching vibration peak at 1668 cm⁻¹ for the C=N of free imidazole has a red shift in the complex, indicating that the N atom is involved in the coordination [24]. The bands at 622 and 477 cm⁻¹ are







attributed to (Sb–N) bond and (Sb–O) bond stretching vibration peak, respectively.

Thermal decomposition process: The thermal stability of the complexes were examined representatively by thermogravemetric analysis (TG) in nitrogen atmosphere from room temperature to 600 °C at a heating rate of 10 °C min⁻¹. The results are shown in Figs. 5 and 6. The data of possible thermal decomposition processes are listed in Table-2. The TG curve of the two complexes display two main steps of weight loss. Fig. 5 shows, the first weight loss of 6.99 % in TG curve occurs between 60 °C and 320 °C in the complex [Sb(Hphth)₂Cl]·2H₂O, corresponding to the loss of two water molecules. The theoretical weight loss (6.88 %) of water molecules is much closed to experimental weight loss. The second weight loss of the complex from 320 to 580 °C is observed about 74.19 % and it is due to the elimination of one third antimony trichloride molecules and the oxidative decomposition of two phthalate hydrogen radical ligands, the experimental weight loss is close to the calculated one (74.56 %). This is consistent with the volatility of antimony chloride. The weight loss of the complex remains constant about 460 °C and the final residue is only

[Sb(Hphth) ₂ Cl]·2H ₂ O AND [Sb(Hphth)(Im)Cl ₂]·H ₂ O							
Reaction	Peak temp. in	Weight loss (%)					
	DTG (°C)	Wexp	W _{theor}				
[Sb(Hphth) ₂ Cl]·2H ₂ O							
$\downarrow -2H_2O$	165, 315	6.99	6.88				
[Sb(Hphth) ₂ Cl]							
\downarrow –(HOOCC ₆ H ₄ CO) ₂ , –1/3SbCl ₃	417	74.19	74.56				
1/3Sb ₂ O ₃		18.82ª	18.56°				
[Sb(Hphth)(Im)Cl ₂]·H ₂ O							
$\downarrow -H_2O$	40	4.21	4.06				
[Sb(Hphth)(Im)Cl ₂]							
\downarrow –Im, –Cl ₂	256	62.90	63.10				
\downarrow –H ₂ O, –		22.003	an oth				
$1/2(C_6H_4COOCOC_6H_4C)_2O$		32.89	32.84°				
$1/2Sb_2O_3$							

TABLE-2 THERMAL DECOMPOSITION DATA OF THE COMPLEXES [Sb(Hphth),Cl1:2H,O AND [Sb(Hphth)(Im)Cl_1]:H,O

^aThe experimental weight percent of the residue in the sample.



is only antimonyous oxide and the experimental result (18.82 %) is in agreement with the result of theoretical calculation (18.56 %). These results further ascertain that composition of the complex is $[Sb(Hphth)_2CI]\cdot 2H_2O$.

Fig. 6 shows that one water molecule is lost when heating the complex from 40 to 125 °C. This accounts for 4.21 % weight loss observes in TG curve. The theoretical weight loss (4.06 %) of one water molecule is much closed to the experimental weight loss. The second weight loss of the complex [Sb(Hphth)(Im)Cl₂]·H₂O occurs between 150 °C and 270 °C. It is due to the elimination and oxidative decomposition of imidazole and phthalate hydrogen radical ligands. The experimental weight loss of 62.90 % is close to the calculated one (63.10 %). The complex is decomposed completely about 270 °C. The final residue is antimonyous oxide and the experimental result (32.89 %) is in agreement with the result of theoretical calculation (32.84 %). These results further ascertain the complex is composed of [Sb(Hphth)(Im)Cl₂]·H₂O.

Conclusion

Two antimony(III) complexes were synthesized with antimony trichloride, phthalic acid and imidazole as main raw materials by solid solid 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 results demonstrate that the deprotonated carboxy group oxygen atoms of phthalate and nitrogen atom of imidazole are coordinated directly to antimony(III) ion in the complexes. The thermal decomposition processes of the complexes under nitrogen included dehydration and pyrolysis of the ligands and the final residue was antimonous oxide. Room temperature solid state synthesis method can be get much higher yield, more inexpensive, faster reaction rate and easier operating and save energy and environmental friendly.

A C K N O W L E D G E M E N T S

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