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SYNTHESIS, CRYSTAL STRUCTURE AND THERMAL DECOMPOSITION OF SOLID COMPLEX

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Abstract

New solid complex of nitrilotriacetic acid and bismuth trichloride was synthesized by a solid phase reaction of nitrilotriacetic acid and bismuth trichloride at room temperature. The composition of the sample is $BiCl_3[N(CH_2COOH)_3]_{2.5}$. The crystal structure of the complex belongs to triclinic system with the lattice parameters: a=0.7849 nm, b=0.9821 nm, c=2.0021 nm, α=96.50°, β=98.76° and γ=90.49°. The far-infrared spectra show the bonding between the Bi ion and N atom of nitrilotriacetic acid. The thermal analysis also demonstrates the complex formation between the bismuth ion and nitrilotriacetic acid. The gaseous pyrolysis product and the final residue in the thermal decomposition process are determined to check the thermal decomposition reaction.

Keywords: crystal structure, nitrilotriacetic acid complex of bismuth, solid phase synthesis, thermal decomposition

Introduction

The main group elements, such as antimony and bismuth, can possess a certain biologic or medicinal properties [1–6] and some complexes of the antimony and bismuth can also treat the cancer [7, 8]. Therefore, to synthesize the new complexes of the bismuth ion and various organic ligands is very interesting not only for the main group element chemistry, but also for the bioinorganic and pharmaceutical chemistry.

To synthesize the solid complexes of the organic ligands and bismuth ion by the aqueous solution reaction is rather difficult, because the inorganic salts of the bismuth ion are very easily hydrolyzed in the aqueous solution [9]. The solid–solid reaction is a simple synthesis method. However, the solid–solid reactions are often carried out at high temperature. We have found that some inorganic salts of bismuth ion and some organic ligands can also react very easily at room temperature. We synthesized some new solid complexes of antimony(III) and bismuth(III) by the solid–solid reaction at room temperature [10]. Here, we shall report the solid–solid reaction syn-

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thesis process of a new solid complex of nitrilotriacetic acid and bismuth trichloride, the crystal structure, far-infrared spectra and thermal decomposition of the complex.

Experimental

All the chemicals used in the experiments are analytical reagent. First, to weigh 0.942 g (3.0 mmol) $BiCl_3$ and 1.439 g (7.5 mmol) $N(CH_2COOH)_3$ and very well to mix up the two reactants together. The molar ratio of $BiCl_3$ to $N(CH_2COOH)_3$ was 1:2.5. Carefully to grind the mixture in an agate mortar. At first the mixture became slightly viscous, then, gradually became a white loose powder. This indicated that the reaction did happen. The reaction conducted in grinding at room temperature for about 8 h. In the end, the resultant was dried in a vacuum drying oven. The resultant is polycrystalline and shows slightly moisture in air.

Carbon, hydrogen and nitrogen in the resultant were determined by an Elementar Vario EL elemental analysis. The content of bismuth in the resultant was measured by the EDTA titration method. The relative content of the element: C (theor. 22.71%; found 23.8%), H (theor. 2.86%; found 3.00%), N (theor. 4.40%; found 4.56%) and Bi (theor. 26.35%; found 25.94%), respectively. The element analyses yield the composition $BiCl_3 \cdot C_{15}H_{22.5}N_{2.5}O_{15}$ of the resultant.

The powder X-ray diffraction pattern of the resultant was recorded by a D/max-YB X-ray diffractometer, $CuK_{\alpha1}$ radiation, scanning rate $2°(2\theta)\ min^{-1}$, at room temperature. The results of indexing to the X-ray diffraction pattern are listed in Table 1. The far-infrared spectra of the resultant and nitrilotriacetic acid were measured by a Nicolet 5D-FT spectrometer and the cesium iodide disk technique. The far-infrared spectra of the resultant and nitrilotriacetic acid in the region from 50 to 650 cm^{-1} are shown in Fig. 1. The thermal decomposition process of the resultant was studied by a LCT-1 differential thermal balance in air, with a heating rate of 10°C min^{-1} and α-Al_2O_3 reference. The thermogravimetric and differential thermal analysis curves of the resultant are shown in Fig. 2. The possible pyrolysis reactions, experimental and calculated percentage mass losses in the thermal decomposition process for the resultant are summarized in Table 2.

Results and discussion

All the diffraction peaks in the pattern can be readily indexed by a set of lattice parameters according to triclinic system, although the number of the diffraction peaks is more. As Table 1 shows, the largest relative deviation between the calculated and experimental d_{hkl} is also less than 0.3%. This indicates that the product of the reaction is a single phase compound with triclinic symmetry. The crystal structure of bismuth trichloride belongs to orthorhombic system (JCPDS 24-1003) and of nitrilotriacetic acid belongs to monoclinic system (JCPDS 44-1941). The crystal structure of the resultant belongs neither to orthorhombic nor to monoclinic system, but to triclinic system. Obviously, the resultant must be a new complex with the triclinic symmetry and the

Table 1 The experimental data and the calculated results for powder X-ray diffraction pattern of $BiCl_3[N(CH_2COOH)_3]_{2.5}$ triclinic system: a=0.7849 nm, b=0.9821 nm, c=2.0021 nm α=96.50°, β=98.76°, γ=90.49°

h, k, l	d_{exp}/nm	d_{cal}/nm	I/I_0	*h, k, l*	d_{exp}/nm	d_{cal}/nm	I/I_0
0 1 2	0.7394	0.7396	45	1 4 3	0.2206	0.2206	27
0 2 1	0.4512	0.4512	22	3 0 4	0.2113	0.2111	5
1 1 2	0.4414	0.4417	40	3 2 5	0.1986	0.1988	7
2 1 2	0.3684	0.3684	18	1 5 0	0.1947	0.1947	31
1 1 5	0.3445	0.3449	100	0 5 1	0.1881	0.1883	9
2 1 3	0.3117	0.3124	18	0 5 2	0.1834	0.1834	22
1 2 5	0.2992	0.2985	19	2 4 3	0.1720	0.1718	8
1 3 1	0.2819	0.2817	5	4 2 1	0.1694	0.1691	26
1 2 4	0.2735	0.2732	73	2 2 8	0.1661	0.1665	19
1 3 1	0.2676	0.2675	91	0 6 1	0.1575	0.1575	32
0 2 7	0.2579	0.2581	11	1 5 5	0.1525	0.1527	10
1 3 5	0.2549	0.2548	6	1 6 4	0.1376	0.1378	11
0 1 8	0.2458	0.2458	12	1 7 2	0.1266	0.1268	11
0 0 8	0.2446	0.2449	16	2 7 5	0.1231	0.1229	9
0 4 2	0.2408	0.2409	6	0 8 0	0.1200	0.1199	4
1 4 1	0.2376	0.2375	6	0 7 7	0.1168	0.1167	5
0 3 5	0.2321	0.2321	5	2 8 5	0.1100	0.1099	7

formula $BiCl_3[N(CH_2COOH)_3]_{2.5}$. However, we have also found that the complex with the composition $BiCl_3$:$N(CH_2COOH)_3$=1:2 can not be obtained by same method.

Table 2 Thermal decomposition data of $BiCl_3[N(CH_2COOH)_3]_{2.5}$

Reaction	T/°C	Mass loss/%	
		W_{exp}	W_{theor}
$BiCl_3[N(CH_2COOH)_3]_{2.5}$ $-3HCl$	236 (endo)	14.1	13.8
$BiN(CH_2COO)_3[N(CH_2COOH)_3]_{1.5}$ $-1.5N(CH_2COOH)_3$	265 (exo)	37.7	36.2
$BiN(CH_2COO)_3$ $-CH_2COO$	417 (exo)	7.3	7.3
$BiN(CH_2COO)_2$ $-0.5[OOCH_2CNCH_2C{-}O{-}CH_2CNCH_2COO]$	521 (exo)	11.1	13.3
Bi_2O_3		29.8*	29.4**

*The percentage mass of the residue in the sample
**The percentage content of Bi_2O_3 in the sample

The absorption peaks from the vibrations of the chemical bonds between the heavy metal ion and the organic ligands are in the far-infrared region. Figure 1 shows that the far-infrared spectra of the complex and nitrilotriacetic acid are very similar, except that there is a new absorption peak at 521 cm^{-1} in the far-infrared spectrum of the complex. The absorption peak from the stretching vibration of the Bi–N bond is at 497 cm^{-1} and of the Bi–O bond is at 443 cm^{-1} in the complex of hexamethylenetetramine and bismuth ion, respectively [10]. The frequency (521 cm^{-1}) of the new absorption peak in the far-infrared spectrum of the complex is closer to that (497 cm^{-1}) of the stretching vibration of the Bi–N bond. Therefore, we can assign the new absorption peak at 521 cm^{-1} probably to the stretching vibration of the chemical bond between the bismuth ion and nitrogen atom of the nitrilotriacetic acid. In the far-infrared spectrum of the gaseous bismuth trichloride molecule, there are 4 characteristic absorption peaks: u_1=342 cm^{-1} and u_3=322 cm^{-1} from the symmetric and asymmetric stretching vibration of the Bi–Cl bond, u_2=123 cm^{-1} and u_4=107 cm^{-1} from the symmetric and asymmetric deformation vibration of the Cl–Bi–Cl bond, respectively [11]. However, the 4 characteristic absorption peaks of the bismuth trichloride molecule do not appear in the far-infrared spectrum of the complex. Of course, we can not rule out that the 4 characteristic absorption peaks and some characteristic absorption peaks of the nitrilotriacetic acid may overlap each other in the far-infrared spectrum of the complex. But, if this does so, some absorption peaks in the far-infrared spectrum of the complex must become appreciable wider than the corresponding absorption peaks in the far-infrared spectrum of the nitrilotriacetic acid or some new shoulders near the main absorption peaks in the far-infrared spectrum of the com-

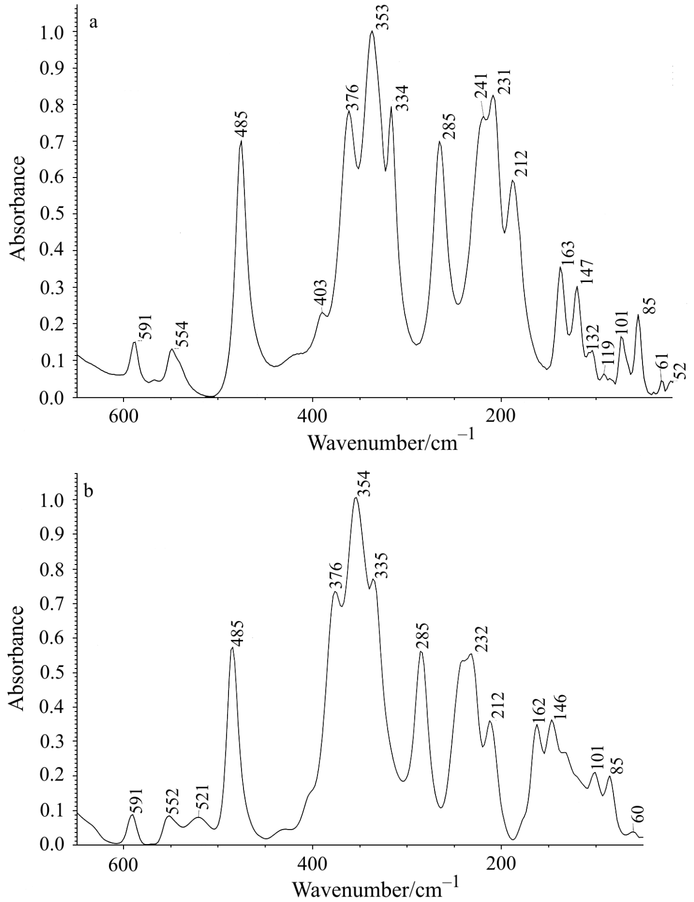

Fig. 1 The far-infrared spectra of a – $N(CH_2COOH)_3$ and b – $BiCl_3[N(CH_2COOH)_3]_{2.5}$

plex should appear, because the position of the 4 characteristic absorption peaks of the bismuth trichloride molecule are different from the position of the characteristic absorption peaks of the nitrilotriacetic acid in the infrared spectra. However, as Fig. 1 shows, the shapes and widths of all the absorption peaks in the far-infrared spectrum of the complex are very similar to those in the fra-infrared spectrum of the nitrilotriacetic acid. So, it is possible that there are no Bi–Cl bonds in the complex or the bonding between the bismuth ion and chloride anion in the complex becomes rather weak. Besides, we have also noted that no absorption peak from the vibration of the Bi–O bond can be found in the far-infrared spectrum of the complex. This means the absence of the bonding between the bismuth(III) and the oxygen atoms of the carboxylic group of the nitrilotriacetic acid. If the above conclusions are reasonable, the far-infrared spectra indicate that the bismuth ion is coordinated neither to the chlorine atoms nor to the oxygen atoms, but only to the nitrogen atoms of the nitrilotriacetic acid in the complex.

Figure 2 shows that the first mass loss of the sample begins at about 230°C. The experimental mass loss (14.1%) indicates the losing of 3HCl molecules (the calculated percentage mass loss: 13.8%). The elimination of the HCl molecules from the complex needs certain energy. Therefore, there is a considerable endothermic peak at about 236°C in DTA curve. To check if the pyrolysis product is the hydrogen chloride gas, a certain amount (about 50 mg) of the complex is placed in a glass test-tube and is slightly heated. The quality of the gaseous decomposition product is detected by using a wet pH paper and a wet paper containing $AgNO_3$. The test demonstrates that the pyrolysis product is an acid gas, while its reaction with $AgNO_3$ gives AgCl. The fact that all the chlorine atoms are very easily eliminated from the complex at such a low temperature, as 230°C, may refer to uncoordinated chlorine anions in the complex. This observation may also support the conclusion of the far-infrared spectrum of the compound. Namely, that there are no Bi–Cl bond vibration peaks in the far-infrared spectrum of the complex. The second mass loss of the sample occurs at about 265°C and there is a small exothermic peak in DTA curve. It is due to the elimination of 1.5 moles of the neutral ligands from the complex. The experimental mass loss (about 38%) is close to the calculated one (36.1%). In the thermal decomposition process, the reaction of the pyrolysis products and the oxygen in air leads to an exothermic peak in DTA curve. The loss of the neutral nitrilotriacetic acids from the complex seems to show that the oxygen atoms of the carboxyl groups of the nitrilotriacetic acids are not bonded directly to the bismuth ion. In that case the sample would gradually lose the CH_2COO groups with increasing temperature. The experimental mass loss for the elimination of the CH_2COO group agrees with the calculated value (7.3%). The elimination of the uncoordinated CH_2COO group from the $N(CH_2COO)_3$ is conducted more easily than that of the N atom from the $N(CH_2COO)_3$ group. This experimental observation supports the proposition that the nitrogen atom of the $N(CH_2COO)_3$ group, and not the oxygen atom of the $N(CH_2COO)_3$

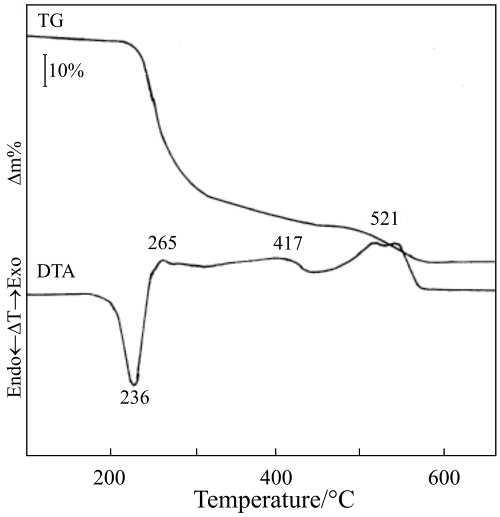

Fig. 2 TG and DTA curves of $BiCl_3[N(CH_2COOH)_3]_{2.5}$

group, is coordinated directly to the bismuth ion. This also corresponds with the far-infrared spectrum of the complex. Namely, in the spectrum of the compound only the absorption peak from the Bi–N vibration is detected, but that from the Bi–O vibration is not present. When the temperature becomes higher, structural rearrangement between the atoms in the residual sample may take place and probably the Bi(III) shall bond to the oxygen atoms of the residual ligand. When the temperature is above 500°C, at first the residue loses two CH_2COO groups, then, it loses the NCH_2COCH_2CN group. Both the CH_2COO and NCH_2COCH_2CN groups can react with the oxygen in air. This is just why two exothermic peaks appear continuously in DTA curve. Finally, the end product of the pyrolysis is Bi_2O_3. To check the final residue, a certain amount of the complex is placed in an alumina crucible and is heated gradually from room temperature to 500°C in a muffule furnace. Then, the sample is kept for 5 min at 520°C. The chemical analysis of the obtained yellow powder indicates that the residue is Bi_2O_3.

Conclusions

New solid complex of bismuth trichloride and nitrilotriacetic acid can be synthesized through a solid–solid reaction of the nitrilotriacetic acid and bismuth trichloride at room temperature. The composition of the sample is $BiCl_3[N(CH_2COOH)_3]_{2.5}$. The crystal structure of the complex belongs to a triclinic system. The far-infrared spectra and the thermal analysis indicate a complex formation between the Bi(III) and N atom of the nitrilotriacetic acid.

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