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 BiCl3[N(CH2COOH)3]2.5. The crystal structure of the complex belongs to triclinic system with the lattice parameters: \( a = 0.7849 \text{ nm} \), \( b = 0.9821 \text{ nm} \), \( c = 2.0021 \text{ nm} \), \( \alpha = 96.50^\circ \), \( \beta = 98.76^\circ \) and \( \gamma = 90.49^\circ \). 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) BiCl₃ and 1.439 g (7.5 mmol) N(CH₂COOH)₃ and very well to mix up the two reactants together. The molar ratio of BiCl₃ to N(CH₂COOH)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 BiCl₃·C₁₅H₂₂.₅N₂.₅O₁₅ of the resultant.

The powder X-ray diffraction pattern of the resultant was recorded by a D/max-YB X-ray diffractometer, CuKα1 radiation, scanning rate 2°(2θ) 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-Al₂O₃ 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 dₜₜ values 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