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Preparation of new amino acid complex nanoparticles of bismuth and leucine

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Summary. The new amino acid complex nanoparticles of bismuth and leucine can be prepared very easily by a room temperature solid–solid reaction. The various characterizations indicate that the formula of the complex is $BiCl[(CH_3)_2CHCH_2CHNH_2COO]_21.5H_2O$. The crystal structure of the solid complex belongs to monoclinic system with the lattice parameters: $a = 1.6036$ nm, $b = 1.9903$ nm, $c = 2.1979$ nm and $\beta = 108.06°$. The new solid complex is nanoparticles with average size about 80 nm.

Keywords: Leucine complex of bismuth – Nanoparticles – Room temperature solid–solid reaction preparation

Introduction

The complexes of the amino acids and metal ions are a kind of important bioinorganic compounds and are widely used to biology and medicine. A lot of bioinorganic complexes of the natural amino acids and various transition metal ions have been prepared. By comparison, the complexes of the main group metal ions and other organic ligands are not more (Singh et al., 1994; Eveland et al., 1996; Siddigui et al., 1996; Bowmarker et al., 1998; Braiannd et al., 1998). Especially, the research on the complexes of the main group metal ions and the amino acids is rather less. Preparations of the nanoparticles have attracted much attention because of some special properties of the nanoparticles. Various nanoparticles have been used in science and technology. Recently, the biologic nanoparticles are also used to medicine. The complexes of the main group metal ions, such as antimony and bismuth ions, can possess a certain biologic function (Cantos et al., 1993; Kopf-Maier et al., 1988). Therefore, to prepare the bioinorganic complex nanoparticles of the bismuth and various amino acids will be interesting not only for the biologic chemistry of main group metal elements, but also for the medicinal application of the amino acid complex nanoparticles. The inorganic salts of the bismuth ion are easily hydrolyzed in the aqueous solution (Greenwood, 1997). Generally, the bismuth will exist as the cation in the acidic aqueous solution, whereas, exist as the anion in the basic aqueous solution. Many amino acids are weak acid. Such amino acids can very well be dissociated only in the basic aqueous. If the acidity of the aqueous solution is larger, although the bismuth can exist as a cation, most of the amino acid molecules are not dissociated. If the aqueous solution is basic, although the amino acid molecules can give the dissociated amino acid anion, the bismuth also exists as the anion in the solution. Therefore to prepare the solid complexes of the bismuth ion and the amino acids through a liquid–liquid reaction in the aqueous solution is often more difficult. The solid–solid reaction is a simple preparation method and has been used to prepare various solid compounds. But, the general solid–solid reaction must be carried out at high temperature. Recently, we find that the bioinorganic complexes of the bismuth and some amino acids can prepared very easily by a room temperature solid–solid reaction. Especially, the resultant prepared by this method is the crystalline nanoparticles. The reports about preparation of the amino acid complexes of bismuth have been less. Up-to-date, no research on the preparation of the crystalline nanoparticles of amino acid complex of bismuth by a room temperature solid–solid reaction is reported. Perhaps, this method may also be used to prepare the nanoparticles of various amino acid complexes of other metal ions. In this letter, we shall report the room temperature solid–solid reaction preparation process and characterization of the new solid complex nanoparticles of bismuth and leucine.

Preparations and methods

Preparation of the solid complex $(CH_3)_2CHCH_2CHNH_2COOLi$: First, to dissolve a certain amount of $LiOH \cdot H_2O$ and $(CH_3)_2CHCH_2CHNH_2COOH$ in anhydrous methanol. The molar ratio is 1:1. The reaction conducted with stirring for about 5 h. Then, the clear solution can be obtained by filtration. Concentrating the filtrate solution got the solid complex. To dry the solid complex in vacuum for 4 h, the white polycrystalline powders can be obtained.

Preparation of the complex of bismuth and leucine: To weigh 1.392 g (4.4 mmol) $BiCl_3$ and 1.695 g (12.4 mmol) $(CH_3)_2CHCH_2CHNH_2COOLi$, respectively. The molar ratio of $BiCl_3$ to $(CH_3)_2CHCH_2CHNH_2COOLi$ is 1:2.8. The two-reactant powders were placed in an agate mortar and mix up. Carefully to grind the mixture in an agate mortar, the reaction conducted at room temperature. At first, the mixture was soaked by a little amount of anhydrous methanol and the mixture became slightly viscous. Then, the mixture gradually became more and more loose. The reaction held for about 8 h. Last, the mixture became white loose powders. To wash the mixture by anhydrous methanol and to test the chlorine ion in the washed solution by the $AgNO_3$ solution. The mixture was washed repeatedly by anhydrous methanol until the content of the chlorine ion in the washed solution did not change. At least, the resultant was dried in vacuum for 4 h. The resultant is white fine powders. Unlike the $BiCl_3$ powders, the resultant powders do not show appreciable moisture.

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 EDTA titration method.

To prepare the single crystal sample by the solid–solid reaction is rather difficult, therefore, we have to measure the powder x-ray diffraction pattern of the resultant to determine if the resultant is crystalline and which crystal system the resultant may belong to. The powder x-ray diffraction pattern of the resultant was recorded by a D/max 2550 VB/PC x-ray diffractometer, $CuK_{\alpha 1}$ radiation at room temperature. The x-ray diffraction pattern is shown in Fig. 1. The results of the indexing for the x-ray diffraction pattern are given in Table 1. For comparison, the powder-x-ray diffraction pattern of $(CH_3)_2CHCH_2CHNH_2COOLi$ was also recorded. The x-ray diffraction pattern and the results of the indexing for the x-ray diffraction pattern are given in Fig. 2 and Table 2, respectively.

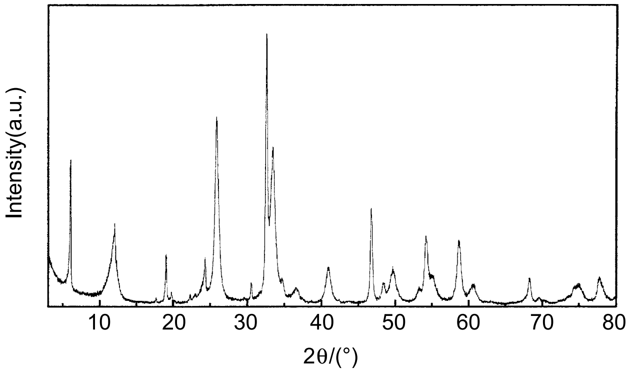

Fig. 1. The x-ray diffraction pattern of $BiCl[(CH_3)_2CHCH_2CHNH_2COO]_2 \cdot 1.5H_2O$

The electron diffraction image of the resultant was obtained by a JEM-200 CX transmission electron microscopy and is shown in Fig. 3. The TEM picture of the resultant was also obtained by a JEM-200 CX transmission electron microscopy. TEM picture is given in Fig. 4.

Results

The element analyses indicate that the relative content of the element: C(theor. 27.09%; found. 26.21), H(theor. 5.08%; found. 4.79%), N(theor. 5.26%; found. 5.07%) and Bi(theor. 39.32%; found 39.76%), respectively. So, the composition of the resultant is $BiClC_{12}H_{27}N_2O_{5.5}$. The most possible formula of the resultant will be $BiCl[(CH_3)_2CHCH_2CHNH_2COO]_2 \cdot 1.5H_2O$. Of course, we can not rule out that the resultant may be a dimer, that is, the formula of the resultant will be $Bi_2Cl_2L_4 \cdot 3H_2O$, $L = (CH_3)_2CHCH_2CHNH_2COO^-$. If this is so, the config-

Table 1. The experimental and calculated data for x-ray diffraction pattern of $BiCl[(CH_3)_2CHCH_2CHNH_2COO]_2 \cdot 1.5H_2O$ (monoclinic system. a = 1.6036 nm, b = 1.9903 nm, c = 2.1979 nm, β = 108.06°)

d_{cal}(nm)	d_{exp}(nm)	h k l	I/I_0	d_{cal}(nm)	d_{exp}(nm)	h k l	I/I_0
1.4671	1.4666	1 0 −1	46	0.2199	0.2200	0 9 1	12
0.7335	0.7345	2 0 −2	25	0.1943	0.1941	8 2 −5	35
0.5005	0.5006	2 3 0	2	0.1877	0.1877	7 −6 −4	4
0.4657	0.4657	2 3 1	18	0.1831	0.1832	1 −6 9	9
0.4492	0.4484	0 4 2	3	0.1718	0.1718	7 −1 5	5
0.3981	0.3986	0 5 0	2	0.1692	0.1691	6 9 −4	19
0.3870	0.3870	3 0 −5	1	0.1665	0.1666	3 9 6	8
0.3658	0.3656	3 3 −4	12	0.1571	0.1572	6 −2 8	22
0.3441	0.3439	4 2 −4	65	0.1523	0.1524	6 7 6	5
0.3016	0.3016	1 −6 −3	1	0.1374	0.1374	9 8 1	9
0.2923	0.2924	2 6 −3	6	0.1350	0.1349	8 −1 8	2
0.2746	0.2746	1 −1 7	100	0.1273	0.1274	9 7 5	3
0.2678	0.2679	2 −5 −6	51	0.1264	0.1265	9 9 3	5
0.2580	0.2581	4 5 −5	7	0.1227	0.1227	8 −5 9	8
0.2455	0.2455	1 8 0	4				

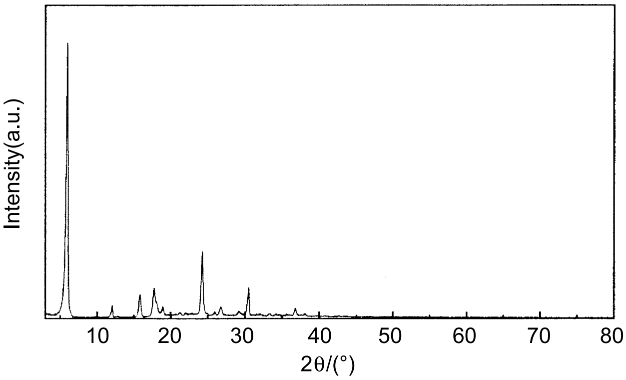

Fig. 2. The x-ray diffraction pattern of $(CH_3)_2CHCH_2CHNH_2COOLi$

uration of the complex $Bi_2Cl_2[(CH_3)_2CHCH_2CHNH_2COO]_4 \cdot 3H_2O$ may possess a bridging structure.

From the results in Table 1, we can find that all the diffraction peaks in the pattern can be very readily indexed by a set of lattice parameters according to the monoclinic symmetry. Especially, the largest relative deviation between the calculated and experimental d_{hkl} is much less than 0.5%, although the number of diffraction peaks is more. This indicates that the resultant does be a single-phase compound. Table 2 shows that the crystal structure of $(CH_3)_2CHCH_2COOLi$ belongs to orthorhombic system. The crystal structure of $BiCl_3$ also belongs to orthorhombic system (JCPDS 24-1003). However, the crystal structure of the resultant belongs to monoclinic system. Obviously, the resultant must be a new polycrystalline compound. The crystal state of the resultant can also be demonstrated by the electron diffraction image.

As Fig. 3 shows, the Debye rings in the selected-area electron diffraction image are very clear and fine. Carefully to check the Debye rings, one can find that the Debye rings are composed of many fine white spots. Such electron diffraction image can demonstrate that the solid complex does be a crystal state compound.

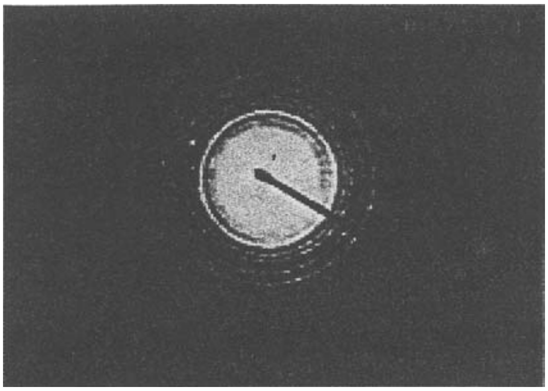

Fig. 3. The selected-area electron diffraction image of $BiCl[(CH_3)_2CHCH_2CHNH_2COO]_2 \cdot 1.5H_2O$

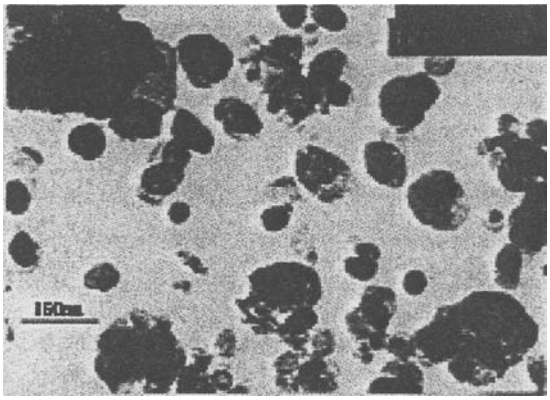

Fig. 4. The transmission electron micrographs of $BiCl[(CH_3)_2CHCH_2CHNH_2COO]_2 \cdot 1.5H_2O$

From the powder x-ray diffraction pattern of the $BiCl[(CH_3)_2CHCH_2CHNH_2COO]_2 \cdot 1.5H_2O$, we can find that the diffraction peaks are considerably widened. After some necessary corrections, from the widening of the diffraction peaks, we can approximately evaluate the average size of the resultant particles by Scherrer formula. The calculations indicate that the solid complex may be

Table 2. The experimental and calculated data for x-ray diffraction pattern of $(CH_3)_2CHCH_2CHNH_2COOLi$ (orthorhombic system. a = 0.7501 nm, b = 1.4695 nm, c = 2.0440 nm)

d_{cal}(nm)	d_{exp}(nm)	h k l	I/I_0	d_{cal}(nm)	d_{exp}(nm)	h k l	I/I_0
1.4695	1.4719	0 1 0	100	0.3661	0.3660	1 2 4	23
0.7347	0.7322	0 2 0	4	0.3424	0.3426	2 1 2	1
0.6914	0.6887	0 2 1	1	0.3319	0.3328	0 1 6	3
0.5592	0.5590	1 1 2	8	0.3035	0.3049	1 1 6	1
0.4996	0.4995	0 2 3	10	0.2920	0.2926	0 0 7	10
0.4898	0.4891	0 3 0	5	0.2699	0.2688	0 5 3	1
0.4669	0.4681	1 2 2	3	0.2432	0.2439	0 6 1	3
0.4195	0.4179	0 2 4	1	0.2367	0.2361	3 2 0	1
0.4021	0.4033	1 3 1	1				

nanoparticles and the average size of the particles may be less than 100 nm.

TEM picture in Fig. 4 shows, indeed, the solid complex is the spherical particles with average diameter of about 80 nm, although the slight aggregation phenomenon between the particles can be observed.

Discussion

Why can the complex nanoparticles of bismuth and leucine be very easily prepared by a solid–solid reaction at room temperature? The above reaction is a chemically replacement reaction. The reaction between the $BiCl_3$ and $(CH_3)_2CHCH_2CHNH_2COOLi$ molecules is mainly to exchange the Bi and Li ions. In principle, if the resultant molecules are thermodynamically more stable than the reactant molecules, the replacement reactions between the reactant molecules can occur. Unlike at the high temperature solid–solid reaction, the diffuse of the atom in the solid is rather slow at room temperature. The room temperature solid–solid reaction occurs only between the molecules on the interface layers of the reactant particles. Hence, the room temperature solid–solid reaction is mainly a surface reaction. In the reaction process of the $BiCl_3$ and $(CH_3)_2CHCH_2CHNH_2COOLi$ powders, after the molecules on the interface layers of the two reactant particles exchange the Bi and Li ions, the resultants will be peeled off right away from the surface of the reactant particles due to grinding the reactant powders. Therefore, the primary resultants in a room temperature solid–solid reaction will be some molecular groups. The structural arrangement or crystallization in the molecular groups can also occur in the reaction process due to the heat effect of the reaction. Perhaps, this is why the crystalline nanoparticles of the complex of bismuth and leucine can be obtained very easily by a room temperature solid–solid reaction. $BiCl_3$ as well as LiCl produced in the above solid–solid reaction are much more easily solubilized in anhydrous methanol than the produced complex. Basing on difference of the solubilities of the reactants and resultants in the anhydrous methanol, we can obtain the pure expected complex through repeatedly washing the reaction mixture by anhydrous methanol.

In summary, the solid complex of bismuth and leucine can very easily prepared by the room temperature solid–solid reaction. The various characterizations indicate that the solid complex obtained by this method is the crystalline nanoparticles with average diameter of about 80 nm. Unlike the high temperature solid–solid reaction, the room temperature solid–solid reaction is mainly a surface reaction. Therefore, the nanoparticles of the leucine complex of bismuth can be prepared by this method. Perhaps, this method can also be used to prepare the nanoparticles of other amino acid complexes of some metal ions.

Acknowledgements

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