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SYNTHESIS, CHARACTERIZATION AND THERMAL DECOMPOSITION OF NEW COMPLEXES OF *p*-METHYL-, *p*-TRIFLUOROMETHYL- AND *p*-BROMO-PHENYLALANINE WITH COPPER

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New bioinorganic complexes of non-natural amino acids (*p*-methyl-, *p*-trifluoromethyl-, *p*-bromo-phenylalanine) and divalent copper ion are synthesized. The crystal structure of the complex of *p*-methylphenylalanine and copper belongs to monoclinic system and that of *p*-trifluoromethyl- or *p*-bromo-phenylalanine and copper belongs to orthorhombic system. The infrared spectra can demonstrate the complex formation. The large difference of the magnetic susceptibilities and of the thermal decomposition processes of the complexes shows that the bonding or coordination structure in the complexes may be different.

Keywords: *characterization, copper complex, non-natural amino acid, synthesis, thermal decomposition*

Introduction

The bioinorganic complexes of amino acids and metal ions are a kind of important inorganic compounds. A lot of complexes of natural amino acids and various metal ions have been synthesized. Now, the number of non-natural amino acids is much more than that of natural amino acids. The non-natural amino acids containing different substitution groups possess some special properties. The various kinds of non-natural amino acids have widely been used to biology, biochemistry and medicine [1–4]. However, the complexes of non-natural amino acids and metal ions are much less than the complexes of natural amino acids and metal ions. To study how the non-natural amino acid and metal ion can form the complex will be helpful for application of the non-natural amino acids. The copper is one of the essential metal elements for life. The complexes of copper and various amino acids were reported [5–8]. The synthesis process for the complex of the non-natural amino acids and metal ion may be different from that of the natural amino acid and metal ion due to special properties of non-natural amino acid with different substitution group. *p*-Methyl-, *p*-trifluoromethyl- and *p*-bromophenylalanine

$$(CH_3C_6H_4CH_2CHNH_2COOH$$
$$CF_3C_6H_4CH_2CHNH_2COOH$$
$$BrC_6H_4CH_2CHNH_2COOH)$$

are the derivatives of alanine and not dissoluble in aqueous solution. The Cu complexes of these amino acids can not be synthesized by a general method. In this paper, we will report the synthesis process of the complex of *p*-methyl-, *p*-trifluoromethyl- or *p*-bromo-phenylalanine and divalent copper ion, the crystal structure, infrared spectra and magnetic susceptibilities of the complexes. Because thermal decomposition can be used to study the complexes of copper [9–11]. We have also measured thermal decomposition processes of the complexes to study the coordination structure or bonding between the amino acid and copper ion in the complexes.

Experimental

The chemicals used in synthesis are the analytical reagent grade. *p*-Methylphenylalanine is levorotatory stereoisomer, *p*-trifluoromethyl- and *p*-bromophenylalanine are dextrotrotatory. First, the aqueous solution of copper nitrate was prepared and the concentration of copper ion was calibrated by EDTA titration. The concentration of the Cu ion is 0.2215 mol L^{-1}. The complex of Cu and *p*-methyl- or *p*-trifluoromethylphenylalanine was synthesized by solid–liquid reaction: to add 1.145 g *p*-methylphenylalanine or 0.990 g *p*-trifluoromethylphenylalanine to 25 mL aqueous solution of copper nitrate. pH of the solution is about 2–3. After the white powders of amino acids were added to the copper nitrate solution, the color of the surface of powders changed to blue indicating that a reaction occurred. During the reaction the lumps of powder were broken up with a glass rod. The solid–liquid reaction conducted at room temperature and held for 2 days. The resultant was collected by filtration and washed

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first by the dilute nitric acid solution pH=3, then by the distilled water and alcohol. The resultant is solubilized in neither alcohol nor acetone. Finally, the resultant was dried in a vacuum desiccator over phosphorus oxide for a week. The complex of Cu and *p*-bromophenylalanine was synthesized by liquid reaction: First, 0.937 g *p*-bromophenylalanine was solubilized in 4 mL (2 mol L^{-1}) NaOH aqueous solution and the solution was diluted by 20 mL distilled water. Then, 20 mL aqueous solution of copper nitrate was added to the above solution by slow drop-wise. Consequently, the blue powdered precipitation was formed. pH of the mixed solution was 4 due to the copper ion being kept in stoichiometric excess. The precipitation was collected by filtration and washed repeatedly with the distilled water. The precipitation is solubilized in neither alcohol nor acetone. Finally, the precipitation was dried in a vacuum desiccator over phosphorus oxide for a week. The resultant is light blue.

The contents of carbon, hydrogen and nitrogen in the resultants were determined by an Elementar Vario EL elemental analyzer and that of copper was determined by EDTA titration.

Characterization of X-ray diffraction for the resultants was carried out by a D/max-YB X-ray diffractometer, $CuK_{\alpha 1}$ radiation; scanning rate is 2(2θ)/min at room temperature. The lattice parameters were refined by a least squares refinement program. The lattice parameters and calculated and experimental spacing d_{hkl} for the Cu complex of *p*-methyl-, *p*-trifluoromethyl- and *p*-bromophenylalanine are listed in Tables 1–3, respectively. Infrared spectra of the complexes in the range of 2000–4000 cm^{-1} were recorded by a Nicolet 5SXC spectrometer and the KBr-disc method. The infrared spectra of the complexes are shown in Fig. 1. Magnetic susceptibilities of the complexes were measured by Faraday method and CTP-F82 magnetic balance at room temperature. The magnetic data of the complexes are given in Table 4. Thermal analysis was performed by a LCT-1 differential thermal balance in air, a heating rate of 10°C min^{-1} and the α-Al_2O_3 reference. The sample mass was 11.6, 5.9 and 7.6 mg for the Cu complex of *p*-methyl-, *p*-trifluoromethyl- and *p*-bromophenylalanine, respectively. The possible pyrolysis reactions in the thermal decomposition processes of the complexes, the experimental and calculated results are summarized in Table 5.

Results and discussion

The elemental analyses indicate that the composition for the Cu complex of *p*-methyl-, *p*-trifluoromethyl- and *p*-bromophenylalanine is $C_{20}H_{27}N_2O_{5.5}Cu$, $C_{20}H_{21}F_6N_2O_{5.5}Cu$ and $C_{18}H_{18}Br_2N_2O_4Cu$, respectively. Therefore, the formula of the complex will be $[CH_3C_6H_4CH_2CHNH_2COO]_2Cu{\cdot}1.5H_2O$ $[CF_3C_6H_4CH_2CHNH_2COO]_2Cu{\cdot}1.5H_2O$ and $[BrC_6H_4CH_2CHNH_2COO]_2Cu$

All the peaks in the X-ray diffraction pattern of each resultant can be very readily indexed by a set of lattice parameters. As Tables 1–3 show, most of the relative deviations between the calculated and experimental spacings are much less than 0.5%. This means that each resultant is the single phase compound.

Figure 1 shows that there are two strong absorption peaks at 3200–3300 cm^{-1} in the infrared spectrum of each complex. The two absorption peaks can be assigned to the characteristic peaks from the antisymmetric and symmetric stretching vibration of the N–H bond in the amino group of complex of amino

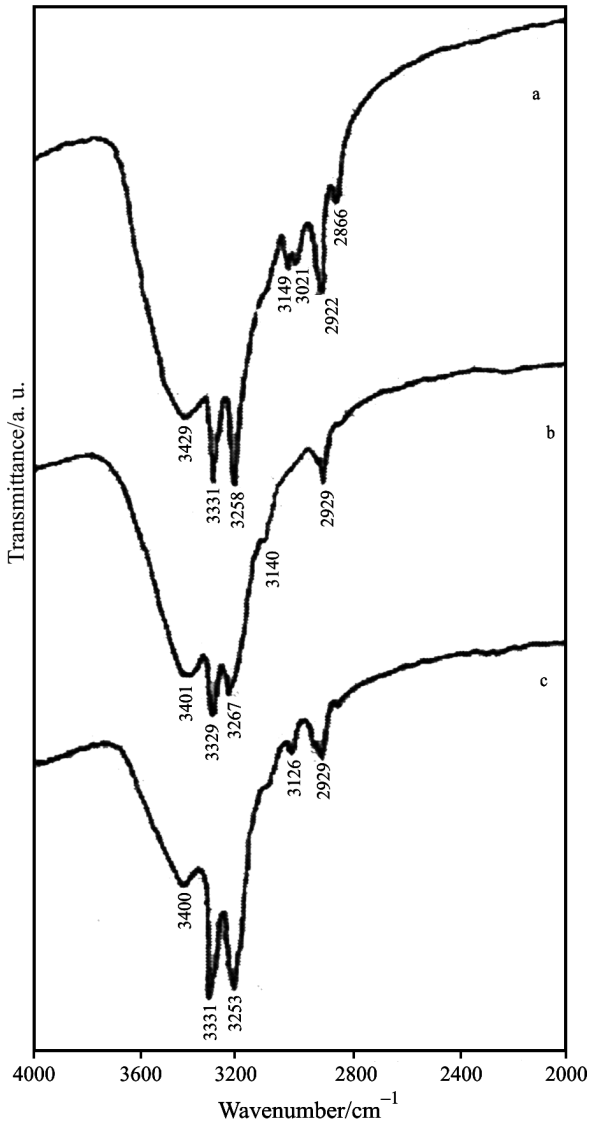

Fig. 1 Infrared spectra of the Cu complex of *p*-methyl-, *p*-trifluoromethyl- and *p*-bromophenylalanine; a – complex of *p*-methylphenylalanine and copper, b – complex of *p*-trifluoromethylphenylalanine and copper, c – complex of *p*-bromophenylalanine and copper

Table 1 The experimental and calculated results for the X-ray diffraction pattern of $(CH_3C_6H_4CH_2CHNH_2COO)_2Cu\cdot 1.5H_2O$; (monoclinic; a=0.9813 nm, b=1.3904 nm, c=1.91202 nm, β=99.68°)

h k l	d_{exp}/nm	d_{cal}/nm	*h k l*	d_{exp}/nm	d_{cal}/nm
0 0 1	1.8866	1.8848	–1 3 5	0.2912	0.2906
0 0 2	0.9361	0.9424	3 2 1	0.2826	0.2826
1 0 2	0.6241	0.6246	–1 0 7	0.2714	0.2715
–1 2 2	0.5052	0.5067	–2 2 6	0.2650	0.2648
0 0 4	0.4741	0.4712	–1 4 5	0.2549	0.2543
2 1 0	0.4567	0.4568	3 0 4	0.2473	0.2474
–2 1 2	0.4405	0.4394	1 5 3	0.2419	0.2419
2 0 2	0.4044	0.4036	–1 6 0	0.2254	0.2254
2 2 0	0.3955	0.3970	–4 1 5	0.2185	0.2184
–1 1 5	0.3607	0.3603	–2 6 1	0.2093	0.2094
2 2 2	0.3509	0.3491	3 2 6	0.1993	0.1994
–2 3 1	0.3356	0.3363	–3 5 7	0.1755	0.1755
–2 1 5	0.3160	0.3165	0 8 3	0.1675	0.1675
–1 4 3	0.2972	0.2972			

Table 2 The experimental and calculated results for the X-ray diffraction pattern of $(CF_3C_6H_4CH_2CHNH_2COO)_2Cu\cdot 1.5H_2O$; (orthorhombic; a=0.9558 nm, b=1.5177 nm, c=1.5302 nm)

h k l	d_{exp}/nm	d_{cal}/nm	*h k l*	d_{exp}/nm	d_{cal}/nm
0 0 1	1.5278	1.5302	2 3 3	0.2870	0.2871
1 0 0	0.9563	0.9558	0 5 2	0.2826	0.2821
0 2 0	0.7609	0.7589	3 2 2	0.2736	0.2742
1 0 2	0.6005	0.5973	3 1 3	0.2677	0.2660
1 2 1	0.5535	0.5540	0 5 3	0.2612	0.2608
0 0 3	0.5169	0.5161	2 1 5	0.2541	0.2541
0 3 0	0.5052	0.5059	0 6 1	0.2499	0.2496
1 2 2	0.4721	0.4694	3 3 3	0.2383	0.2383
1 0 3	0.4516	0.4500	1 2 6	0.2343	0.2344
2 1 2	0.3914	0.3916	2 1 6	0.2229	0.2226
0 0 4	0.3811	0.3826	0 5 5	0.2156	0.2155
0 4 1	0.3657	0.3683	0 2 7	0.2105	0.2101
1 1 4	0.3448	0.3458	0 7 3	0.1995	0.1995
0 2 4	0.3414	0.3416	0 5 6	0.1951	0.1953
2 3 2	0.3153	0.3163	0 7 4	0.1889	0.1886
0 5 0	0.3026	0.3035	3 5 5	0.1785	0.1784
2 4 1	0.2917	0.2921	2 8 2	0.1720	0.1718

acid and metal ion [12]. If this assignment is correct, there must be a certain relationship between the frequency (υ_{as}) of antisymmetric stretching vibration and that (υ_s) of symmetric stretching vibration: υ_s=345.5+0.876υ_{as} [12]. If to assume υ_{as}=3331, 3329 and 3331 cm^{-1} in infrared spectra of the Cu complex of *p*-methyl-, *p*-trifluoromethyl- and *p*-bromophenylalanine, respectively, the calculated υ_s will be 3263, 3262 and 3263 cm^{-1}. Obviously, the calculated υ_s is close to the experimental υ_s (3258, 3267 and 3253 cm^{-1}). The free amino acid exists as an inner salt. Therefore, there are always both protonated amino group ($-NH_3^+$) and deprotonated carboxyl group ($-COO^-$) in any free amino acid [13]. However, the amino group ($-NH_2$) can exist only in the complex of amino acid and metal ion. So, the presence of characteristic absorption peaks from the antisymmetric and symmetric stretching vibration of the N–H bond in the amino group ($-NH_2$) can demonstrate the formation of the complex.

Table 3 The experimental and calculated results for the X-ray diffraction pattern of $(BrC_6H_4CH_2CHNH_2COO)_2Cu$; (orthorhombic; a=0.8816 nm, b=1.6888 nm, c=1.8601 nm)

h k l	d_{exp}/nm	d_{cal}/nm	*h k l*	d_{exp}/nm	d_{cal}/nm
0 0 1	1.8628	1.8601	0 4 6	0.2499	0.2499
0 0 2	0.9263	0.9300	2 2 6	0.2431	0.2429
0 2 0	0.8402	0.8444	1 4 6	0.2405	0.2404
0 2 2	0.6312	0.6252	3 2 4	0.2378	0.2383
0 0 3	0.6180	0.6200	1 3 7	0.2316	0.2318
0 3 0	0.5612	0.5629	0 5 6	0.2286	0.2284
0 2 3	0.4979	0.4998	1 1 8	0.2234	0.2229
0 1 4	0.4476	0.4483	4 0 1	0.2191	0.2189
0 4 1	0.4137	0.4117	4 1 1	0.2165	0.2171
1 1 4	0.3998	0.3996	4 1 2	0.2123	0.2128
0 1 5	0.3633	0.3633	2 3 7	0.2105	0.2110
1 4 2	0.3537	0.3524	0 6 6	0.2083	0.2084
1 0 5	0.3435	0.3428	2 0 8	0.2057	0.2057
1 1 5	0.3366	0.3359	0 2 9	0.2007	0.2008
2 0 4	0.3202	0.3199	0 8 3	0.1999	0.1998
0 5 2	0.3166	0.3175	4 3 3	0.1945	0.1948
0 0 6	0.3085	0.3100	2 2 9	0.1823	0.1827
2 4 1	0.3006	0.3009	1 5 9	0.1727	0.1729
0 3 6	0.2714	0.2716	0 3 11	0.1615	0.1620
1 6 0	0.2684	0.2681	0 8 8	0.1564	0.1563
2 5 1	0.2645	0.2654	0 8 9	0.1478	0.1477
3 3 1	0.2582	0.2580	5 4 6	0.1440	0.1441

Table 4 The magnetic data of the complexes

Complex	Cu-*p*-methylphenylalanine	Cu-*p*-trifluoromethylphenylalanine	Cu-*p*-bromophenylalanine
[a]exp/emu g^{-1}	$5.16\cdot10^{-6}$	$2.46\cdot10^{-6}$	$1.25\cdot10^{-6}$
M/g mol^{-1}	446.6	554.6	549.5
[b]M/emu mol^{-1}	$2.304\cdot10^{-3}$	$1.364\cdot10^{-3}$	$0.687\cdot10^{-3}$
[c]diam/emu mol^{-1}	$-0.267\cdot10^{-3}$	$-0.247\cdot10^{-3}$	$-0.263\cdot10^{-3}$
[d]para/emu mol^{-1}	$2.571\cdot10^{-3}$	$1.611\cdot10^{-3}$	$0.950\cdot10^{-3}$

[a]exp – the experimental susceptibility of sample, M – the molecular mass of the complex, [b]M – the experimental molar susceptibility, [c]diam – the molar diamagnetic susceptibility, [d]para – the real molar paramagnetic susceptibility

As Table 4 shows, all the complexes are paramagnetic. After diamagnetic correction for the experimental magnetic susceptibility by Pascal's constants [14], the paramagnetic susceptibility decreases appreciably from the Cu complex of the *p*-methyl-, *p*-trifluoromethylphenylalanine to the Cu complex of *p*-bromophenylalanine. The paramagnetic susceptibility of the complex depends mainly on the magnetic ion or the bonding in the complex. The difference between the paramagnetic susceptibilities means that the number of the unpaired electrons at the Cu ion or the bonding between the Cu ion and ligands in the complexes will be different. The induction effect can explain why the Cu complex of *p*-methylphenylalanine has larger paramagnetic susceptibility than that of *p*-trifluoromethylphenylalanine. Because fluorine has very large electronegativity (3.98), the trifluoromethyl group can lead a larger induction effect. Therefore, in the Cu complex of *p*-trifluoromethylphenylalanine, more electrons will move from the Cu ion to the ligands. However, the induction effect can not explain why the Cu complex of *p*-trifluoromethylphenylalanine possesses larger paramagnetic susceptibility than that of *p*-bromophenylalanine, because the electronegativity (2.96) of bromine is much smaller than that (3.98) of fluorine. It is reported that the iodine atoms may directly coordinate

Table 5 Thermal decomposition data of $(CH_3C_6H_4CH_2CHNH_2COO)_2Cu\cdot1.5H_2O$, $(CF_3C_6H_4CH_2CHNH_2COO)_2Cu\cdot1.5H_2O$ and $(BrC_6H_4CH_2CHNH_2COO)_2Cu$

Reaction	Temperature/°C	Total mass loss/%	
		M_{exp}	$M_{theor.}$
$(CH_3C_6H_4CH_2CHNH_2COO)_2Cu\cdot1.5H_2O$ $\downarrow -1.5H_2O$	>50 (endo)	6.1	6.0
$(CH_3C_6H_4CH_2CHNH_2COO)_2Cu$ $\downarrow -2C_6H_4$	239 (exo)	32.9	34.0
$(CH_3CH_2CHNH_2COO)_2Cu$ $\downarrow -2NH, CO_2$	380 (exo)	16.4	16.6
$(CH_3CH_2CH_2)_2COOCu$ $\downarrow -CH_2CH_2CH_3$	450 (exo)	9.1	9.6
$CH_3CH_2CH_2COOCu$ $\downarrow$ –d.p.	525 (exo)	16.4	15.9
CuO		19.1*	17.8**
$(CF_3C_6H_4CH_2CHNH_2COO)_2Cu\cdot1.5H_2O$ $\downarrow -1.5H_2O$	100 (endo)	5.0	4.9
$(CF_3C_6H_4CH_2CHNH_2COO)_2Cu$ $\downarrow -2NH$	135 (exo)	5.6	5.4
$(CF_3C_6H_4CH_2CH_2COO)_2Cu$ $\downarrow -2C_6H_4$	220 (exo)	27.5	27.5
$(CF_3CH_2CH_2COO)_2Cu$ $\downarrow -2CF_3$	380 (endo)	25.5	24.9
$(CH_2CH_2COO)_2Cu$ $\downarrow$ –d.p.	460 (exo)	21.5	23.0
CuO		14.9*	14.3**
$(BrC_6H_4CH_2CHNH_2COO)_2Cu$ $\downarrow -2C_6H_4$	210 (exo)	27.2	27.6
$(BrCH_2CHNH_2COO)_2Cu$ $\downarrow -2NH, CO_2$	400 (exo)	13.5	13.5
$(BrCH_2CH_2)_2COOCu$ $\downarrow$ –d.p.	510 (exo)	15.1	15.3
BrOCuBr $\downarrow -2Br$	580 (exo)	30.2	29.1
CuO		14.0*	14.5**

d.p. – decomposition product,
* – the percentage mass of the residue in the sample,
** – the percentage content of CuO in the complex.

to the metal ion in the complexes of the Cu, Co and Ni ions with some non-natural amino acids [15, 16]. If assuming that the Br atom can also directly coordinate to the Cu ion in the solid complex, we can understand why the paramagnetic susceptibility of the Cu complex of *p*-bromophenylalanine is smaller than that of *p*-trifluoromethylphenylalanine. Because the electronegativity (1.98) of copper is much smaller than that (2.96) of bromine, more 3d electrons of the Cu ion will move to the Br atom when the Br atom directly coordinates to the Cu ion. The effect of direct coordination on the electron population at the Cu ion is much larger than that of the induction effect. Perhaps, this is also just why the paramagnetic susceptibility of the Cu complex of *p*-bromophenylalanine is smaller than that of *p*-trifluoromethylphenylalanine. If this does be so, the complexes may possess different coordination structure. We have also noted that the Cu complex of *p*-trifluoromethyl- or *p*-methylphenylalanine contains 1.5 water molecules. So, we can assume, in the Cu complexes of *p*-trifluoromethylalanine and *p*-methylphenylalanine, the Cu ion will be coordinated both by four O atoms from the two carboxyl groups ($-COO^-$) and by the O atoms from the water molecules. Of course, we can not rule out that the Cu complex of *p*-trifluoromethyl- or *p*-methylphenylalanine may be a dimer. In this case, the composition of the complex will be $Cu_2L_4\cdot3H_2O$. The configuration of the dimer may possess the bridging bonds composed of the Cu ion and the O atoms. The Cu complex of *p*-bromo-

phenylalanine does not contain any water molecule. Because the highest coordination number of the Cu ion can be 6, perhaps, we can assume, in the Cu complex of *p*-bromophenylalanine, the Cu ion will be coordinated not only by four O atoms from the two carboxyl groups ($-COO^-$), but also by two Br atoms from the *p*-bromophenylalanine molecules, like in some complexes of the metal ions with the non-natural amino acids [15, 16]. The thermal decomposition process of the complex can demonstrate this conclusion.

The first mass loss of the Cu complex of *p*-methylphenylalanine is from dehydration. The experimental mass loss (6.1%) indicates the presence of 1.5 water molecules (theoretical mass 6.0%). Because the sample has been dried in a vacuum desiccator over phosphorus oxide for a week, the water molecules must be the lattice water. A larger mass loss and the exothermic peak at 239°C in DTA curve correspond to the elimination of phenylene group from the ligand. The pyrolytic elimination of $-NH_2$ and decarboxylation will successively occur in a range of 300 to 400°C. Above 400°C, the sample will lose $CH_3CH_2CH_2O-$ group corresponding the exothermic peak at 450°C in DTA curve. The experimental mass loss (9.1%) is very close to the theoretical one (9.6%). Last, the sample loses the residual ligand at above 500°C and there is a larger exothermic peak at 525°C in DTA curve. A similar mass loss from dehydration is also observed in TG curve of the Cu complex of *p*-trifluoromethyl-phenylalanine. The experimental mass loss (5.0%) consists with the percentage content (4.9%) of 1.5 water molecules in the complex. But, unlike the Cu complex of *p*-methylphenylalanine, the Cu complex of *p*-trifluoromethylphenylalanine loses first the $-NH_2$ and phenylene group. The experimental mass loss (5.6% and 27.5%) agrees well with the theoretical one (5.4 and 27.5%). Then, the sample loses the $-CF_3$ group corresponding a small endothermic peak at 380°C in DTA curve. A large exothermic peak at 460°C in DTA curve is from burning the residual ligand. The residue is CuO. Thermal decomposition process of the Cu complex of *p*-bromophenylalanine shows no presence of the water molecule in the complex. The first mass loss at 200°C is due to thermal elimination of the phenylene group from the ligand. The experimental and theoretical mass loss are 27.2 and 27.6%, respectively, and there is an exothermic peak in DTA curve. Then, the sample loses slowly the amino and carboxyl group. TG curve shows that the residual ligand is eliminated at 500°C, but the bromine can be lost only above 550°C. The agreement of the experimental mass loss (15.1 and 30.2%) with the theoretical one (15.3 and 29.1%) supports the above conclusion. The residue is also CuO. The bond energy (85 kcal mol^{-1}) of C–C bond is larger than that (68 kcal mol^{-1}) of C–Br bond [17]. Especially, the bromine atom is at the terminal site and the phenylene group is in the link of ligand. However, why is the phenylene group in the link eliminated more easily from the ligand than the bromine atom at the termal site? As the above mentioned, it may be because the coordination of the Br atom to the Cu ion can weaken the bonding between the Br and C atom in the benzene ring. In this case, the elimination of the phenylene group from the ligand becomes much more easily than that of the Br atom from the ligand. Therefore, the thermal decomposition process of the Cu complex of *p*-bromophenylalanine can also demonstrate the presence of the coordination bond between the Cu ion and Br atom in the complex. It is be possible that the Br atom at the terminal site of the ligand of a complex molecule in the lattice can be close to and directly coordinated to the Cu ion of another complex molecule in the lattice of the solid complex.

Conclusions

The complexes of *p*-methyl-, *p*-trifluoromethyl-, *p*-bromophenylalanine and divalent copper ion are synthesized by solid-liquid or liquid-liquid reaction. The crystal structure of the Cu complex of *p*-methylphenylalanine belongs to monoclinic system and that of *p*-trifluoromethyl- and *p*-bromophenylalanine belongs to orthorhombic one. The presence of the characteristic absorption peaks from antisymmetric and symmetric stretching vibration of the N–H bond in amino group can demonstrate the complex formation between the Cu ion and amino acid. The magnetic measurement indicates that the complexes are paramagnetic and may possess the different bonding or coordination structure. The dehydration reaction of the Cu complex of *p*-methyl- or *p*-trifluoromethylphenylalanine reveals the presence of the lattice waters. The experimental fact that the bromine atom at the terminal site of the ligand is much more difficult eliminated than the phenylene group in the main chain of the ligand may imply that the terminal Br atom has been coordinated directly to the Cu ion in the lattice of the solid complex of *p*-bromophenylalanine and Cu ion.

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