

## ARTICLE

# Preparation and Spectroscopic Study of Different Stoichiometric Solid Supramolecular Inclusion Complexes of $\beta$ -Cyclodextrin with Short Chain Aliphatic Amines

Le-xin Song\*, Chuan-feng Teng, Hai-ming Wang, Lei Bai

Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

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The solid Supramolecular complexes of  $\beta$ -cyclodextrin ( $\beta$ -CD) with ethylenediamine **1**, diethylenetriamine **2** and triethylamine **3** were obtained and characterized using elemental analysis, powder X-ray diffraction, infrared spectroscopy, thermogravimetric analysis, and  $^1\text{H}$  nuclear magnetic resonance spectroscopy. Based on the results of elemental analysis and  $^1\text{H}$  NMR, the guest-host stoichiometries of the three solid complexes were determined to be 5:2 for **1**- $\beta$ -CD, 1:1 for **2**- $\beta$ -CD, and 1:3 for **3**- $\beta$ -CD. The yields were relative to the molar volume ratio of guest to  $\beta$ -CD cavity, and increased in the order: **1**- $\beta$ -CD < **2**- $\beta$ -CD < **3**- $\beta$ -CD. X-ray diffraction patterns of the inclusion complexes gave very good exhibitions not only in location of diffraction peaks but also in shape and diffraction intensity of the peaks due to the intermolecular complexations between  $\beta$ -CD and the guests. The formation of host-guest inclusion complexes exhibited obviously enhanced phase change temperatures of the complexed guests such as **1** and **3**. The H-5 protons located at the narrower rim inside the CD cavity experienced a higher shift upon inclusion while all other protons experienced lower shifts.

**Key words:**  $\beta$ -cyclodextrin, Inclusion complex, Ethylenediamine, Supramolecular

## I. INTRODUCTION

$\beta$ -Cyclodextrin ( $\beta$ -CD, Fig.1), having a fairly rigid and hydrophobic cavity, can form Supramolecular inclusion complexes with various organic guest molecules or ions [1-4] and continues to be the subject of current interest in basic and applied researches [5-7].

Ethylenediamine **1** and diethylenetriamine **2** are simple diamine and triamine, respectively, having one and two ethyl groups. They are both particularly useful as bidentate or tridentate ligands for forming coordina-

tion compounds with many transition metal ions. As an aliphatic tertiary monoamine, triethylamine **3** is an important organic solvent. The three short aliphatic amines, **1-3** (see Fig.1), are all liquid at room temperature.

Although there are plentiful researches on inclusion complexations of CDs with aromatic guests [6-9], much less attention is paid to the study of the interactions between CDs and aliphatic compounds, especially short chain aliphatic compounds [2,8,10,11]. The preparation and spectroscopic study of solid CD inclusion complexes of guests could reveal valuable information concerning their stoichiometries, structural properties, yields and thermal stabilities, all of which are very important in evaluation of the feasibility for practical application of CD Supramolecular of guests in many industries such as food, pharmaceutical and cosmetic industries [12-14].

In view of the little historical effort on the inclusion complexation of CD with short chain alkyl amines both in solution and in solid state, therefore, the three alkyl amines **1-3** and  $\beta$ -CD were chosen as guests and host, respectively. The preparation of three solid CD inclusion complexes, **1**- $\beta$ -CD, **2**- $\beta$ -CD, and **3**- $\beta$ -CD, are reported here for the first time. Their spectroscopic properties were characterized by using elemental analysis (EA), powder X-ray diffraction (XRD), infrared spectroscopy (IR), thermogravimetric analysis (TG) and  $^1\text{H}$  nuclear magnetic resonance ( $^1\text{H}$  NMR) spectroscopy. An important and interesting inclusion phenomenon concerning the entirely different chemical stoichiometries in the solid supermolecules of  $\beta$ -CD with the three short aliphatic amines was found in the present work.

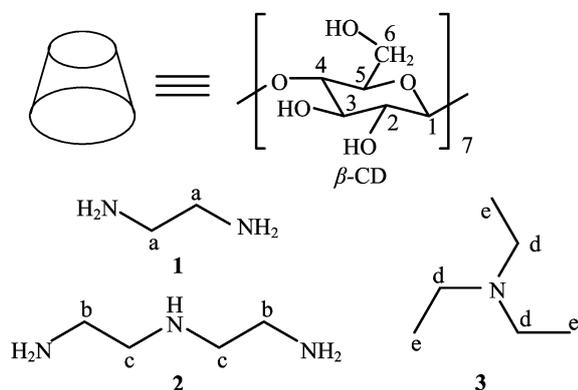


FIG. 1 Molecular structures of  $\beta$ -CD and guests **1-3**.

\* Author to whom correspondence should be addressed. E-mail: solexin@ustc.edu.cn

TABLE I Preparation and properties of the solid inclusion complexes of  $\beta$ -CD with guests **1-3**

Compound	<i>MVR</i> <sup>a</sup>	Yield/%	<i>DP</i> <sup>b</sup> /°C	<i>SR</i> <sup>c</sup>	<i>NWM</i> <sup>d</sup>	$\Delta$ <i>NWM</i> <sup>e</sup>	Composition	Calcd/%			Found/%		
								C	H	N	C	H	N
<b>1</b> - $\beta$ -CD	0.44	54.8	324.1	2:5	4	6	C <sub>94</sub> H <sub>188</sub> N <sub>10</sub> O <sub>74</sub>	42.73	7.12	5.30	42.40	7.16	5.53
<b>2</b> - $\beta$ -CD	0.71	67.6	332.4	1:1	1	7	C <sub>46</sub> H <sub>85</sub> N <sub>3</sub> O <sub>36</sub>	43.98	6.77	3.35	44.16	6.80	3.09
<b>3</b> - $\beta$ -CD	0.86	76.1	323.1	3:1	21	1	C <sub>132</sub> H <sub>246</sub> NO <sub>147</sub>	40.81	6.88	0.36	40.95	6.77	0.49

<sup>a</sup> *MVR* stands for the molar volume ratio of guest molecular to  $\beta$ -CD cavity.

<sup>b</sup> *DP* corresponds to the temperature point of the fastest decomposition process from TG curves of the samples.

<sup>c</sup> *SR* represents the stoichiometric ratio of host to guest in the supermolecule.

<sup>d</sup> *NWM* represents the number of water molecules in the supermolecule.

<sup>e</sup>  $\Delta$ *NWM* is the difference in the *NWM* values between free  $\beta$ -CD and a complexed  $\beta$ -CD, respectively.

## II. EXPERIMENTS

### A. Materials

$\beta$ -CD was purchased from Shanghai Chemical Reagent Company and recrystallized twice from deionized distilled water before use. Three organic guests **1-3** were purchased from Shanghai Chemical Reagent Company and used without further purification. All other chemicals were of general-purpose reagent grade unless otherwise stated.

### B. Preparation of the solid inclusion complexes

The solid inclusion complexes were prepared by mixing a guest into aqueous solution of  $\beta$ -CD (1.00 mmol/dm<sup>3</sup>) with stirring 48 h at 25 °C. A guest/host molar ratio of 10:1 was used in the initial reaction. The crude reaction products were, in turn, washed with deionized distilled water (3×5 mL), anhydrous ethanol (3×3 mL) and diethyl ether anhydrous (3×3 mL). After the solvents were removed under vacuum, the solid inclusion complexes were dried over 24 h at 110 °C *in vacuo*. Three pure solid inclusion complexes, **1**- $\beta$ -CD, **2**- $\beta$ -CD, and **3**- $\beta$ -CD, were obtained and stored in a vacuum desiccator over silica gel until further required. Some of their properties were listed in Table I.

### C. Characterization of the guest- $\beta$ -CD inclusion complexes in solid state

XRD of the solid samples was measured on a Philips X'Pert Pro X-ray diffractometer. These samples were irradiated with monochromatized Cu K $\alpha$  and analyzed with 5° ≤ 2 $\theta$  ≤ 40°. The voltage and current were 40 kV and 40 mA, respectively.

Fourier transform IR spectra were recorded on Bruker EQUINOX55 spectrometer and obtained from KBr pellets in the 4000-400 cm<sup>-1</sup> regions.

TG curves were recorded on Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 10.0 K/min

under a nitrogen atmosphere.

<sup>1</sup>H NMR spectra of the solid samples were obtained on Bruker NMR spectrometer at 300 MHz at 25 °C, using D<sub>2</sub>O as solvent and TMS as internal reference.

Elemental analyses were carried out on an Elementar Vario EL III elemental analyzer.

## III. RESULTS AND DISCUSSION

### A. Preparation analysis

The three supermolecules, **1**- $\beta$ -CD, **2**- $\beta$ -CD, and **3**- $\beta$ -CD, were prepared by a direct compression method [15,16]. Since the three complexes show a very good solubility in aqueous solution, the direct compression method has to be used in the present work. There are few reports on the method used in preparing CD inclusion complexes of simple organic compounds.

Their yields calculated on the basis of the initial concentration of  $\beta$ -CD, thermal decomposition temperatures, compositions and results of elemental analysis are listed Table I.

The stoichiometric ratio (*SR*) of host to guest in the solid Supramolecular complexes was determined to be 2:5 for **1**- $\beta$ -CD, 1:1 for **2**- $\beta$ -CD, and 3:1 for **3**- $\beta$ -CD, based on the results of EA (see Table I), and further confirmed by comparing the relative integral areas of the proton signals between  $\beta$ -CD and the guests. This is a very interesting inclusion phenomenon. It does seem inconceivable that the three small guests with slight differences in their molecular structures could cause entirely different values of *SR*. Clearly, the inclusion behavior of the same host to different guests in Supramolecular chemistry is somewhat similar to that of the same central ion to different ligands in coordination chemistry. It is well-known that there are plentiful investigations on coordination numbers of transition metal coordination compounds [17,18]. However, much less attention is paid to the study on "complexation numbers", i.e. *SR*. How to perceive and comprehend the nature and significance of the complexation numbers resulting from intermolecular interactions is still

TABLE II Experimental IR and XRD data of  $\beta$ -CD and its three complexes

Compound	IR/cm <sup>-1</sup>		XRD $2\theta/(\circ)$		
	$\nu_{C-O}$	$\nu_{O-H}$	$I_1$	$I_2$	$I_3$
$\beta$ -CD	1028.7, 1079.8, 1157.4	3389.2, 1416.1	12.6	9.1	22.7
<b>1</b> - $\beta$ -CD	1032.1, 1081.5, 1155.9	3362.9	12.5	9.1	10.7
<b>2</b> - $\beta$ -CD	1031.0, 1080.8, 1156.2	3403.8, 1415.8	12.6	19.3	18.0
<b>3</b> - $\beta$ -CD	1029.1, 1079.1, 1155.9	3413.7, 1411.6	6.6	12.0	17.7

worth emphasizing. Here, we will try to explain the inclusion phenomenon based on the relationship among the yield, *MVR*, *NMW*, and *SR*, firstly.

As shown in Table I, the yield of **1**- $\beta$ -CD (54.8%) is slightly lower than that of **2**- $\beta$ -CD (67.6%), and obviously lower than that of **3**- $\beta$ -CD (76.1%) under the same conditions. In Table I, the values of *MVR* of **1**- $\beta$ -CD, **2**- $\beta$ -CD, and **3**- $\beta$ -CD are 0.44, 0.71, and 0.86, respectively. This observation suggests that the smaller the differences between the molecular volumes of short alkyl amine and the size of  $\beta$ -CD cavity are, the higher the yields of the host-guest inclusion complexes prepared will be.

Of the three guests, the guest molecule **1** has the smallest molecular volume (69.0 cm<sup>3</sup>/mol) and the lowest value of *MVR*, which make it fail to fully match the free space of  $\beta$ -CD cavity. Therefore, in consideration of the *SR* value in the complex, the five guest molecules in **1**- $\beta$ -CD would have to be accommodated into the cavities of two hosts in order that they can, to the fullest extent, fill the free space of  $\beta$ -CD cavity.

It is worthy of note that *NWM* could be used to investigate the free-space loss of  $\beta$ -CD cavity upon complexation by guests. Free  $\beta$ -CD contains about eight water molecules on the basis of TG analysis under the same dry conditions as the three inclusion complexes. However, in **1**- $\beta$ -CD, the *NWM* value is equal to 4, indicating that the penetration of **1** into the cavity resulted in the release of about six water molecules from each  $\beta$ -CD.

Guest **2** can form a higher yield's complex than guest **1**, possibly because its molecular volume or spatial structure make it more fit for the cavity of  $\beta$ -CD. *NWM* with a value of **1** or  $\Delta$ *NWM* with a value of 7 seems to support this opinion.

Guest **3** with three hydrophobic  $-\text{CH}_2\text{CH}_3$  groups prefers to be bound into the hydrophobic cavities by three  $\beta$ -CD molecules. The water molecules in **3**- $\beta$ -CD would take up much room in the cavities since the molecular volume of **3** is much smaller than the sum of the free space of three cavities. There are only small differences ( $\Delta$ *NWM*=1 for each  $\beta$ -CD) in the *NWM* values before and after inclusion of  $\beta$ -CD for guest **3**. This finding implies that the three side chains ( $-\text{CH}_2\text{CH}_3$ ) of guest **3** do not insert deeply into the cavity of  $\beta$ -CD.

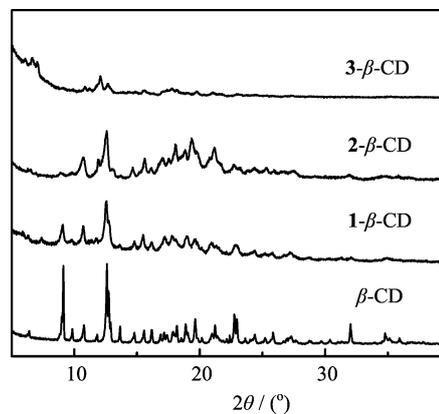


FIG. 2 XRD spectra of powder diffraction.

## B. XRD analysis

Powder XRD analysis has proved to be an effective means to characterize the solid inclusion complexes of CDs with all kinds of guests [13,14]. A set of diffraction patterns consisting of  $\beta$ -CD and its three inclusion complexes is displayed in Fig.2.

Guests **1**, **2**, and **3** are all liquids, so there are no XRD data available. The  $2\theta$  values of the top three peaks ( $I_1$ , the first strongest;  $I_2$ , the second; and  $I_3$ , the third) of each curve in Fig.2 are listed in Table II.

According to the data in Fig.2 and Table II, the solid complexes exhibit significant differences in signal positions ( $2\theta$ ) and relative intensities of  $I_1$ ,  $I_2$ , and  $I_3$ , when compared with free  $\beta$ -CD. The  $I_1$ ,  $I_2$ , and  $I_3$  of free  $\beta$ -CD are located at  $2\theta$  values of 12.6°, 9.1°, and 22.7° respectively.

Obvious discrepancies between the XRD curves of free  $\beta$ -CD and **1**- $\beta$ -CD have been observed. The first strongest peak at  $2\theta$  value of 12.6° ( $I_1$ ) in  $\beta$ -CD is slightly shifted to 12.5° ( $I_1$ ) in **1**- $\beta$ -CD. In addition, the third strongest peak is significantly shifted from 22.7° before inclusion to 10.7° after inclusion.

There are no strong diffraction peaks at  $2\theta < 10^\circ$  in **2**- $\beta$ -CD as shown in Fig.2. And upon complexation, the second strongest peak ( $I_2$ ) at  $2\theta$  value of 9.1° of  $\beta$ -CD disappears almost completely, though the position and intensity of the strongest peak at  $2\theta$  value of 12.6° of  $\beta$ -CD does not show any prominent change before and after inclusion. The second and third strongest peaks

in 2- $\beta$ -CD appear at the  $2\theta$  angular values of  $19.3^\circ$  and  $18.0^\circ$  respectively, which are markedly different from those of free  $\beta$ -CD (see Table II).

Also, it is worth stressing that the positions and relative intensities of the first, second and third strongest peaks in 3- $\beta$ -CD differ almost completely from those of  $\beta$ -CD, and no strong diffraction peaks are found at  $2\theta > 18^\circ$ . The  $I_1$ ,  $I_2$ , and  $I_3$  of 3- $\beta$ -CD are observed at the  $2\theta$  values near  $6.6^\circ$ ,  $12.0^\circ$ , and  $17.7^\circ$  respectively.

Moreover, from Fig.2, it is found that the diffraction curves of the three inclusion complexes of  $\beta$ -CD share a common ground of the more amorphous solid state than free  $\beta$ -CD [19-21]. Furthermore, the shape, intensity and position of the first strongest peak of these complexes except for 3- $\beta$ -CD are very close to those of the first strongest peak of free  $\beta$ -CD. Although the XRD pattern of 2- $\beta$ -CD is somewhat like that of 1- $\beta$ -CD in the range of  $2\theta$  from  $10.5^\circ$  to  $17.0^\circ$ , there are many obvious differences between them as displayed in Fig.2 and Table II. Also, the XRD patterns of 1- $\beta$ -CD and 2- $\beta$ -CD, especially the shape, position and intensity of  $I_1$ ,  $I_2$ , and  $I_3$ , are clearly distinct from that of 3- $\beta$ -CD.

The above results suggest that the intermolecular interactions occurred between  $\beta$ -CD and guests 1-3. Despite the three guests only consisting of ethyl and amino groups, their different shape and size made them form different stoichiometric complexes with  $\beta$ -CD. The trenchant differences in XRD patterns between host and its complex or among these complexes clearly reflect the different structural requirements for the primary, secondary and tertiary aliphatic amines' entry into the cavity of  $\beta$ -CD to form stable solid Supramolecular complexes.

### C. IR spectra analysis

IR data of  $\beta$ -CD and its inclusion complexes are also listed in Table II. Free  $\beta$ -CD has strong absorption bands at  $3417.6$  and  $1028.7$   $\text{cm}^{-1}$ , attributed to  $\nu_{\text{O-H}}$  and  $\nu_{\text{C-O}}$  of  $\beta$ -CD, respectively. Also, there appear a series of peaks superimposed in the range  $820$ - $1180$   $\text{cm}^{-1}$ , which refer to  $\nu_{\text{C-O}}$  and  $\nu_{\text{C-C}}$  stretching modes of  $\beta$ -CD.

IR spectrum of guest 1 displays two sharp peaks at  $3340$  and  $3270$   $\text{cm}^{-1}$ , corresponding to stretching vibration of  $\nu_{\text{N-H}}$  in amino groups, and a sharp peak at  $1095$   $\text{cm}^{-1}$  due to  $\nu_{\text{C-N}}$ . Guest 2 has IR peaks at  $3360$ ,  $3290$ , and  $1125$   $\text{cm}^{-1}$ . Guest 3 has a typical peak at  $1130.0$   $\text{cm}^{-1}$  resulting from  $\nu_{\text{C-N}}$ .

The  $\nu_{\text{C-O}}$  stretching bands of the  $\beta$ -CD complexes of 1-3 are rather similar to one another. As can be seen in Table II, the peaks of  $\nu_{\text{C-O}}$  of 1- $\beta$ -CD appear at  $1032.1$ ,  $1081.5$ , and  $1155.9$   $\text{cm}^{-1}$ , all of which are slightly different from those of 2- $\beta$ -CD and 3- $\beta$ -CD. In addition, they shift only slightly in the range  $1$ - $4$   $\text{cm}^{-1}$ , when compared with those of  $\beta$ -CD at  $1028.7$ ,  $1079.8$ ,

and  $1157.4$   $\text{cm}^{-1}$ .

The results of the EA and XRD studies have revealed that there exists an interaction between  $\beta$ -CD and the three short-chain alkyl amines 1-3, however, the IR peaks of these guests in their complexes of  $\beta$ -CD could not be clearly observed. This may be because the weight proportion of the guests with low molecular weight in inclusion complexes is so small ( $< 9\%$ ) that their intrinsic peaks are basically covered by those of  $\beta$ -CD having high molecular weight [13].

### D. Thermogravimetric analysis

TG curves of  $\beta$ -CD and its inclusion complexes are shown in Fig.3. Because guests 1-3 are all liquids, there are no TG figures available.

In Fig.3(a), the first weight loss of  $10.90\%$  of the  $\beta$ -CD hydrate occurs below around  $110$   $^\circ\text{C}$ , corresponding to water release of about  $7.7$  molecules (calcd.  $7.71$ ). This can be explained as the evaporation of complexed and uncomplexed water from solid  $\beta$ -CD $\cdot 7.7\text{H}_2\text{O}$ . The second weight loss of  $61.23\%$  occurs in the range  $300$ - $350$   $^\circ\text{C}$  due to the single melting-decomposition of  $\beta$ -CD [14].

As shown in Fig.3(b), the TG curve of 1- $\beta$ -CD is distinctly different from that of pure  $\beta$ -CD. The first weight loss of  $3.41\%$  of 1- $\beta$ -CD occurs below  $112$   $^\circ\text{C}$ , indicating the water release of about five molecules (calcd.  $5.03$ ) inside and/or outside the  $\beta$ -CD cavity in the solid complex, 1- $\beta$ -CD. By contrast with  $\beta$ -CD, a new weight loss of  $11.18\%$  appears in the range  $143.6$ - $241.3$   $^\circ\text{C}$ , corresponding with the guest release of about five molecules (calcd.  $4.94$ ), which is in good agreement with the result of EA. This does not happen in the TG curve of pure  $\beta$ -CD, as in Fig.3(a).

The gasification temperature of guest 1 in the  $\beta$ -CD complex is obviously higher than its boiling point of  $117.5$   $^\circ\text{C}$ , strongly suggesting that the intermolecular complexation between 1 and  $\beta$ -CD could effectively improve the thermal stability of the guest. It should be noted that after the guest disappears from its complex, the weight loss of the residue mainly consisting of  $\beta$ -CD begins to occur at about  $242$   $^\circ\text{C}$ . The TG profile concerning the melting/decomposition of the residue in the range  $242$ - $300$   $^\circ\text{C}$  is rather different from that of free  $\beta$ -CD, since the initial decomposition temperature of the latter occurs at above  $290$   $^\circ\text{C}$ . However, a further increase in temperature would lead to a very rapid weight loss of 1- $\beta$ -CD at around  $324.1$   $^\circ\text{C}$ , which is fairly similar to the thermal decomposition of  $\beta$ -CD at  $322.8$   $^\circ\text{C}$ .

As for the TG curve profile of 2- $\beta$ -CD in Fig.3(c), to all appearances, it is somewhat similar to that of 1- $\beta$ -CD, but very different from that of pure  $\beta$ -CD.

The thermal decomposition temperature of the inclusion complex is slightly raised when compared with that of  $\beta$ -CD or 1- $\beta$ -CD. A new weight loss of  $7.47\%$

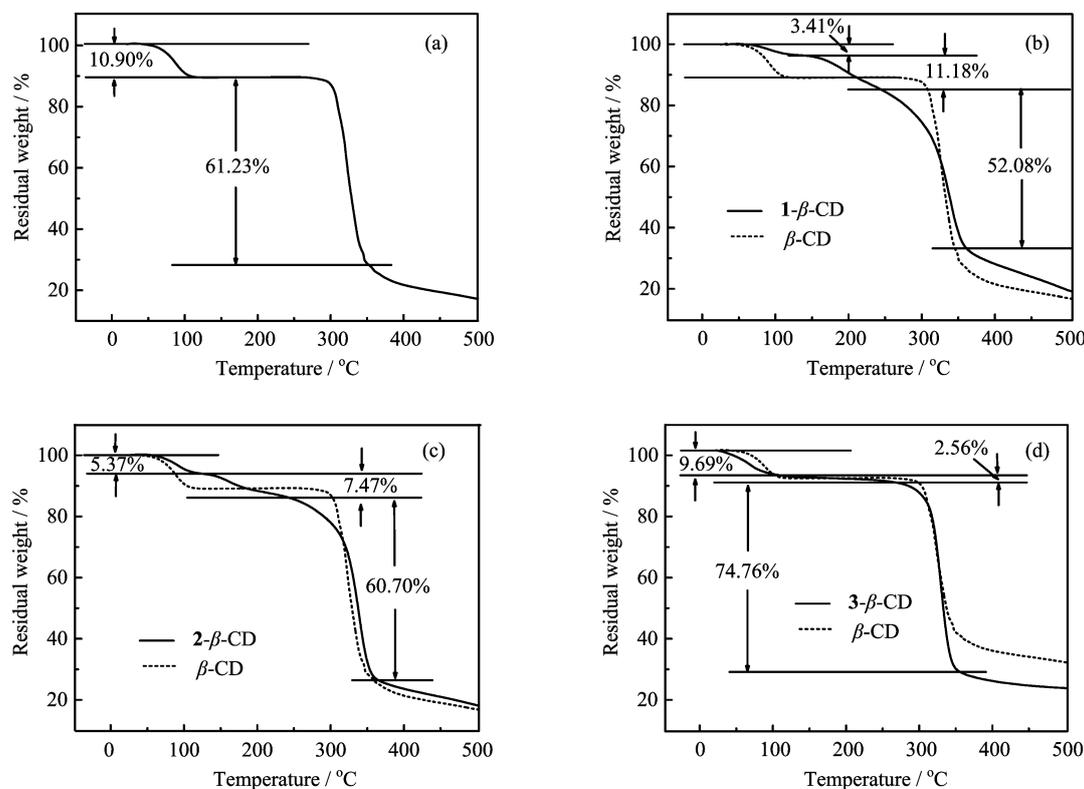


FIG. 3 TG curves of  $\beta$ -CD (a),  $1\text{-}\beta$ -CD (b),  $2\text{-}\beta$ -CD (c), and  $3\text{-}\beta$ -CD (d).

in  $2\text{-}\beta$ -CD was observed in the range  $128.77\text{-}239.09\text{ }^{\circ}\text{C}$  due to the guest release of one molecule (calcd. 0.94). This is a surprising inclusion phenomenon because the initial temperature of phase change or thermal decomposition of the complexed guest **2** is obviously lower than the boiling point of free guest **2** at  $202.0\text{ }^{\circ}\text{C}$ . In other words, the intermolecular complexation between **2** and  $\beta$ -CD quite reduces the thermal stability of guest **2**. Similar phenomena also occur in those TG curves of  $2\text{-}\beta$ -CD, obtained at several different heating rates. This is quite new and weird because extra energy will be always necessary to destroy any intermolecular interaction between host and guest. As far as we know, there have been no reports describing this inclusion behavior. We try to ascribe this phenomenon to different intermolecular interaction intensity: host-guest < guest-guest, i.e.  $\beta\text{-CD-2} < 2\text{-2}$ .

As can be seen in the TG curve profile of  $3\text{-}\beta$ -CD in Fig.3(d), though it shares much resemblance with that of pure  $\beta$ -CD, there are still some differences between them.

After releasing about 21 water molecules (calcd. 20.87) inside or outside the  $\beta$ -CD cavity, the TG figure of  $3\text{-}\beta$ -CD shows a new, very slow weight loss of 2.56% in the range  $110\text{-}260\text{ }^{\circ}\text{C}$ , accompanying the guest release of one molecule (calcd. 0.98). This result about guest weight loss is quite consistent with that of EA measurement.

In view of the boiling point of guest **3** at  $89.5\text{ }^{\circ}\text{C}$ , we conclude that the complexation behavior has the effect of impeding the evaporation of the guest molecule that has penetrated into the cavity of  $\beta$ -CD. This observation indicates the formation of the inclusion complex between  $\beta$ -CD and guest **3**. Furthermore, a very clear, prodigious difference of the residuals between them is found in the range of higher temperature. For example, at  $400\text{ }^{\circ}\text{C}$ ,  $\beta$ -CD and  $3\text{-}\beta$ -CD keeps down 21.55% and 9.61%, respectively, and at  $500\text{ }^{\circ}\text{C}$ , 16.70% and 6.69%, respectively. In other words, when temperature is in the range  $350\text{-}500\text{ }^{\circ}\text{C}$ , the weight of the remains is two times greater in  $\beta$ -CD than in  $3\text{-}\beta$ -CD, reflecting their structural difference in spatial stack or arrangement.

Therefore, it can be concluded from Fig.3 that a new weight loss in the curves of the three inclusion complexes occurred as a result of the release of guest molecules in comparison with that of pure  $\beta$ -CD. The initial thermal decomposition temperatures of these complexes were reduced to some extent, due to the heats of evaporation and decomposition of the complexed guests.

Additionally, as can be seen in Table I and Fig.3, the thermal decomposition points ( $DP$ ) of  $1\text{-}\beta$ -CD ( $324.1\text{ }^{\circ}\text{C}$ )  $2\text{-}\beta$ -CD ( $332.4\text{ }^{\circ}\text{C}$ ), and  $3\text{-}\beta$ -CD ( $323.1\text{ }^{\circ}\text{C}$ ), are slightly higher than that of free  $\beta$ -CD ( $322.8\text{ }^{\circ}\text{C}$ ). Of the three complexes,  $2\text{-}\beta$ -CD is more thermodynamically stable than the other two. Before and after inclu-

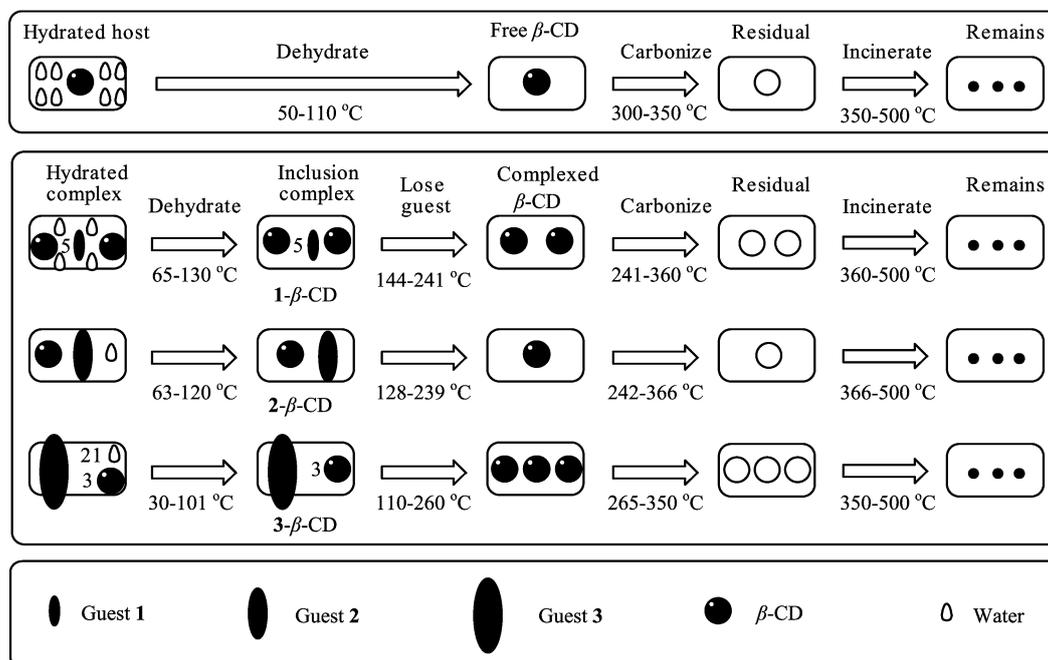


FIG. 4 Consecutive mechanisms depicting the decomposition of  $\beta$ -CD and its complexes:  $1$ - $\beta$ -CD,  $2$ - $\beta$ -CD, and  $3$ - $\beta$ -CD.

sion, no obvious differences in the  $DP$  values of  $\beta$ -CD and  $3$ - $\beta$ -CD at around  $323$  °C are observed.

Figure 4 illustrates four consecutive mechanisms depicting the decomposition of  $\beta$ -CD and its three complexes:  $1$ - $\beta$ -CD,  $2$ - $\beta$ -CD, and  $3$ - $\beta$ -CD. These observations not only clearly indicate the formation of host-guest inclusion complexes, but also reveal that the different strength of intermolecular complexation between  $\beta$ -CD and guests  $1$ - $3$ . Further, the complex formation obviously increases the phase change temperature of guests  $1$  and  $3$ , but considerably decreases the thermal decomposition temperature of guest  $2$ .

### E. $^1\text{H}$ NMR spectra analysis

$^1\text{H}$  NMR is one of most important techniques to examine the host-guest inclusion complexes of CDs with various organic guests in solution [22,23]. The chemical shifts  $\delta$  of both the interior protons of CD cavity and the guest protons are used to provide information concerning inclusion mode and binding affinity between CD and guest.

Based on the relative integral areas of the proton signals between  $\beta$ -CD and guest from  $^1\text{H}$  NMR spectroscopy in Fig.5, the host-guest stoichiometries of  $1$ - $\beta$ -CD,  $2$ - $\beta$ -CD, and  $3$ - $\beta$ -CD are confirmed to be 2:5, 1:1, and 3:1, respectively, which are consistent with the known results from EA. In  $1$ - $\beta$ -CD, five guest molecules were involved in the internal hydrophobic cavities of two  $\beta$ -CD molecules when the inclusion complex formed, showing relatively high complexation numbers of host

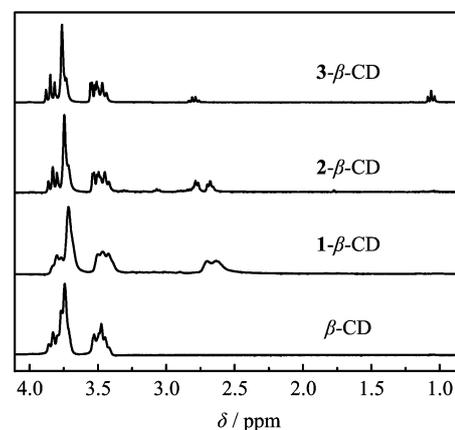


FIG. 5  $^1\text{H}$  NMR spectra of  $\beta$ -CD and its complexes.

due to the small size ( $MVR$ , 0.44) of guest molecule  $1$ . The value of  $MVR$  increases with increasing chain length of alkyl amine, so guest  $2$  is able to form the 1:1 inclusion complex,  $2$ - $\beta$ -CD ( $MVR$ , 0.71). In  $3$ - $\beta$ -CD, one guest molecule was accommodated in the rigid cavities of three  $\beta$ -CD molecules, indicating very low complexation numbers of host due to the big size ( $MVR$ , 0.86) of guest molecule  $3$ . The three ethyl side chains of the alkyl amine, structurally, could allow it simultaneously to penetrate into the cavities of three different CDs.

The changes of chemical shifts  $\Delta\delta$  of the interior protons of  $\beta$ -CD such as H-3 and H-5 have been used not only to demonstrate interactions between CD and guest,

TABLE III  $^1\text{H}$  NMR chemical shifts in  $\text{D}_2\text{O}$  of the C–H protons in  $\beta\text{-CD}$  and guests, and the chemical shift changes  $\Delta\delta$  of  $\beta\text{-CD}$  and guests after inclusion

	$\delta/\text{ppm}$	$\Delta\delta/\text{ppm}$		
	$\beta\text{-CD}$	<b>1</b> - $\beta\text{-CD}$	<b>2</b> - $\beta\text{-CD}$	<b>3</b> - $\beta\text{-CD}$
H-1	4.933	−0.003	0.011	0.026
H-2	3.510	−0.004	0.010	0.027
H-3	3.832	−0.008	0.003	0.020
H-4	3.448	−0.004	0.005	0.027
H-5	3.780	−0.042	0.030	0.044
H-6	3.804	−0.005	0.009	0.037
	$\delta/\text{ppm}$	$\Delta\delta/\text{ppm}$		
	Guests	<b>1</b> - $\beta\text{-CD}$	<b>2</b> - $\beta\text{-CD}$	<b>3</b> - $\beta\text{-CD}$
H-a	2.910	−0.213	–	–
H-b	2.770	–	−0.086	–
H-c	2.810	–	−0.019	–
H-d	2.400	–	–	0.403
H-e	1.000	–	–	0.067

but also to describe structures of  $\beta\text{-CD}$  supermolecules of guests [24,25]. As can be seen in Table III, the proton signals of  $\beta\text{-CD}$  upon inclusion with guest **1** show a small upfield shift, though these signals in **2**- $\beta\text{-CD}$  or **3**- $\beta\text{-CD}$  show a small downfield shift. Moreover, the proton signals of the guests, while complexed in **1**- $\beta\text{-CD}$  and **2**- $\beta\text{-CD}$ , shift to upfield when compared with that of free guest **1** or **2**.

The H-3 chemical shifts in pure  $\beta\text{-CD}$  and **1**- $\beta\text{-CD}$  are 3.832 and 3.824 ppm, respectively, with a  $\Delta\delta$  value of  $-0.008$  ppm. The chemical shifts of H-5 are 3.780 and 3.738 ppm, respectively, with a  $\Delta\delta$  value of  $-0.042$  ppm. The chemical shift changes of other protons between pure  $\beta\text{-CD}$  and **1**- $\beta\text{-CD}$  are fairly small in comparison with those of H-3 and H-5. Furthermore, the chemical shift change of H-5 is much bigger than that of all other protons including H-3, indicating that guest **1** inside the  $\beta\text{-CD}$  cavity might prefer to stay in the narrower rim.

The  $\text{CH}_2$  protons signals of guest **1** after inclusion obviously shift toward upfield from 2.910 ppm to 2.697 ppm, with a big  $\Delta\delta$  value of  $-0.213$  ppm. This observation further confirms that there is a strong intermolecular interaction between  $\beta\text{-CD}$  and guest **1**.

The above phenomena also occur in the inclusion system of guest **2** and  $\beta\text{-CD}$  as shown in Table III. Therefore, it should be reasonable that guests **1** and **2** within  $\beta\text{-CD}$  cavity are close to the primary hydroxyl group of the cavity.

However, the proton signals of the alkyl chains ( $-\text{CH}_2$  and  $-\text{CH}_3$ ) in guest **3** upon inclusion significantly shift toward downfield, suggesting that these protons should be in the unshielded areas [22]. The observation indicates the molecular structure of **3**- $\beta\text{-CD}$  is different from that of **1**- $\beta\text{-CD}$  or **2**- $\beta\text{-CD}$ .

Although the three guests are all very small organic

compounds consisting of simple ethyl and amino groups, they can form three different stoichiometric solid complexes with the same host molecule, clearly reflecting that the spatial structure of guest plays a very important role in the formation of the CD supermolecule of short alkyl amines.

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