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# Molecule-Ion Interaction and Its Effect on Coordination Interaction

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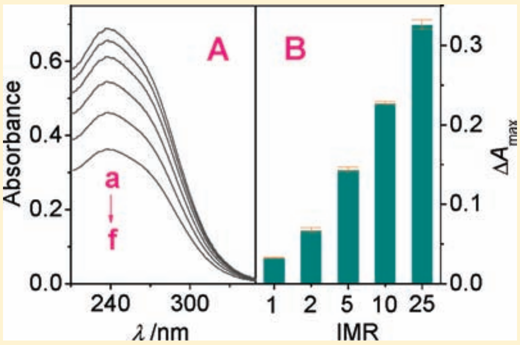
Supporting Information

**ABSTRACT:** The present work revealed the presence of the molecule—ion interaction between ethylenediaminetetraacetic acid disodium salt ($Na_2H_2EDTA$) and $\beta$-cyclodextrin (CD) on the basis of observable changes in crystal patterns and thermal behaviors before and after interaction. Results from electric conductivity measurements confirmed this presence and showed that the extent of the molecule—ion interaction was associated with the concentration of $\beta$-CD. More importantly, the molecule—ion interaction led to a decreased coordination interaction of $Na_2H_2EDTA$ and copper chloride, and this decrease exhibited a concentration dependence of $\beta$-CD. Similar phenomena were also observed in the case of several analogs of $Na_2H_2EDTA$ by UV—vis spectroscopy. A possible explanation was proposed on the basis of the hypothesis that there was a competitive relationship between the molecule—ion interaction and the coordination interaction. Further, nuclear magnetic resonance measurements provided important information on the difference in interaction modes of $\beta$-CD with $H_2EDTA^{2-}$ and $[Cu(EDTA)]^{2-}$. We are of the opinion that the results would provide a significant bridge between coordination chemistry and supramolecular chemistry and help us further understand factors related to different interactions in multicomponent systems.



## INTRODUCTION

$\beta$-Cyclodextrin (CD) is an important macrocyclic host that can form inclusion complexes with many guests such as organic molecules, inorganic compounds, and metal complexes by intermolecular interaction (IMI).[1−4] Over the past few decades, numerous efforts have focused on elucidating the mechanisms involved in this inclusion process between $\beta$-CD and organic guests driven by IMI.[5−8] Rather surprisingly, only a little attention has been paid to the analysis of association process between $\beta$-CD and inorganic or organic salts driven by molecule—ion interaction (MII).[9−11] In recent studies, we obtained data that strongly suggested the involvement of MII in the processes of precipitation—dissolution reactions, thermal decomposition reactions, and heterogeneous catalysis reactions.[12−14] This indicates the importance and necessity of studying this interaction.

As one of most basic types of chemical reactions, metal—ligand coordination interactions (MLCI) have been well recognized and have wide applications, for example, in water treatment,[15] electroplating treatment,[16−18] dyeing auxiliaries, semiconductor materials, blood anticoagulants, enzyme catalysis, and so on.[19−22] In these cases, several interactions such as IMI, MII, and MLCI can coexist simultaneously as shown in Figure 1. Hence, in dealing with data analysis for such a multicomponent system, it is important and necessary to consider the mutual influence of each type of the interactions on the other.

Unfortunately, little historical data was available which would permit us to discuss the importance of the mutual influence. Hence, the present work attempts to construct a framework containing a host, ligand, and metal ion, within which there are two types of interactions: MII and MLCI. $\beta$-CD, ethylenediaminetetraacetic acid disodium salt ($Na_2H_2EDTA$), and copper(II) ion ($Cu^{2+}$) are chosen as the host, ligand, and central metal ion, respectively, to assess effect of MII ($H_2EDTA^{2-}$/$\beta$-CD and $Cu^{2+}$/$\beta$-CD) on MLCI ($Cu^{2+}$/$H_2EDTA^{2-}$).

First, the effectiveness of the MII between $Na_2H_2EDTA$ and $\beta$-CD was well reflected by changes in microstructures, stacking behaviors, and decomposition processes.

Next, addition of $\beta$-CD to an aqueous solution of $Na_2H_2EDTA$ as well as an aqueous solution of copper chloride ($CuCl_2$) and the mixed solution of $Na_2H_2EDTA$ with $CuCl_2$ showed a decrease in electric conductivity ($\kappa$). This provided evidence that there was the MII between $\beta$-CD and each of the components: $Na_2H_2EDTA$, $CuCl_2$, and $[Cu(EDTA)]^{2-}$. Different addition orders of reagents were tested and obvious differences were observed, which was explained as a competitive response to each other in the tricomponent system.

Then, a decreased coordination ability of $Na_2H_2EDTA$ to $Cu^{2+}$ in the presence of $\beta$-CD was observed in UV—vis spectra. This was attributed to the contribution of the MII between $\beta$-CD and $H_2EDTA^{2-}$, as well as between $\beta$-CD and $Cu^{2+}$ to the MLCI between $Cu^{2+}$ and $H_2EDTA^{2-}$. A similar pattern occurred in the case of analogs of $Na_2H_2EDTA$. Further, there was a concentration dependence to the effect of $\beta$-CD on the stability of the coordination compound $[Cu(EDTA)]^{2-}$.

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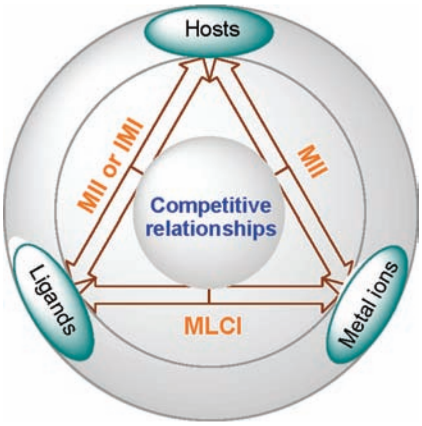

**Figure 1.** Interactions in tricomponent systems.

Finally, the MII between $\beta$-CD and $H_2EDTA^{2-}$, especially the complexation interaction between $\beta$-CD and $[Cu(EDTA)]^{2-}$, was demonstrated by nuclear magnetic resonance (NMR) measurements, and two different interaction modes were observed.

The purpose of the present work is to investigate the competitive relationship between MII and MLCI. We believe that the findings of this research may not only serve as a bridge between coordination chemistry and supramolecular chemistry but also will be significant in assisting the development of other chemical sciences.

## EXPERIMENTAL SECTION

**Materials.** $\beta$-CD was purchased from Shanghai Chemical Reagent Company and recrystallized twice from deionized distilled water. Analytically pure ethylenediaminetetraacetic acid ($H_4EDTA$) and $Na_2H_2EDTA$ were supplied by Chinese Medical Group Shanghai Chemical Reagent Company, Sinopharm Chemical Reagent Co., Ltd. Ethylenediaminetetraacetic acid trisodium salt ($Na_3HEDTA$) and ethylenediaminetetraacetic acid tetrasodium salt ($Na_4EDTA$) were purchased from Tokyo Kasei Kogyo Co., Ltd. and Tianjin Guangfu Fine Chemical Research Institute, respectively. $CuCl_2$ was purchased from Guangdong Xilong Chemical Reagent Company and used as received without further purification. All other chemicals were of general-purpose reagent grade unless otherwise stated.

**Preparation of Solid Samples for Analyzing the Presence of MII between $Na_2H_2EDTA$ and $\beta$-CD.** Solid samples were prepared by mixing $\beta$-CD (1.135 g, 1 mmol) with one of the ligands, for example, $Na_2H_2EDTA$ (0.336 g, 1 mmol) in deionized distilled water of 50 mL into an autoclave and then heating at 393 K for 4 h. After water was removed below 323 K under reduced pressure, and a yellowish residue was dried into a light yellow powder in a vacuum at 393 K. Four solid samples were marked as $H_4EDTA-\beta$-CD, $Na_2H_2EDTA-\beta$-CD, $Na_3HEDTA-\beta$-CD, and $Na_4EDTA-\beta$-CD, all of which were obtained in fine crystal powders and measured under the same drying conditions. Additionally, a physical mixture of $\beta$-CD with $Na_2H_2EDTA$ was prepared by mixing an equimolar ratio of the two reagents.

A small amount of samples of $Na_2H_2EDTA$, $\beta$-CD and $Na_2H_2EDTA-\beta$-CD were dried to a constant weight at 393 K under vacuum. After they were cooled to 298 K in evacuated desiccators over $P_2O_5$, the samples were weighed and calcined for 15 min at 603, 653, 703, 753, and 803 K, under ambient atmosphere in a muffle furnace. Each residue was weighed after it was cooled to 298 K in a desiccator. Residual mass percentages of samples were determined on the basis of the initial masses of the samples at the same drying conditions.

**Preparation of Solution Samples for Confirming the Presence of MII.** Aqueous solutions (2.00, 5.00, 10.00, 20.00, and 30.00 × $10^{-4}$ mol·dm$^{-3}$) of $Na_2H_2EDTA$ as well as $CuCl_2$ were prepared to measure changes of $\kappa$ values in the presence of the same concentrations of $\beta$-CD at 298 K.

An aqueous solution of 1.00 × $10^{-3}$ mol·dm$^{-3}$ of $Na_2H_2EDTA$ as well as $CuCl_2$ and their mixture (1:1, molar ratio) was prepared to evaluate the relationship between the change in $\kappa$ values and the concentration of $\beta$-CD from 0.00 to 1.00 × $10^{-2}$ mol·dm$^{-3}$ at 298 K.

Mixed aqueous solutions of $Na_2H_2EDTA$, $CuCl_2$, and $\beta$-CD at the same concentrations (2.00, 5.00, 10.00, 20.00, and 30.00 × $10^{-4}$ mol·dm$^{-3}$) were prepared in three different addition sequences ($S_1$ to $S_3$) and characterized by measurements of $\kappa$ values at 298 K. $S_1$, aqueous solutions of $Na_2H_2EDTA$ and $CuCl_2$ ,was mixed and stirred for 10 min, and then $\beta$-CD was added to the mixed solutions. $S_2$, aqueous solutions of $Na_2H_2EDTA$ and $\beta$-CD, was mixed and stirred for 10 min, and then $CuCl_2$ was added into the mixed solutions. $S_3$, aqueous solutions of $\beta$-CD and $CuCl_2$, was mixed and stirred for 10 min, and then $Na_2H_2EDTA$ was added into the mixed solutions. All $\kappa$ values related to $\beta$-CD were obtained after deducting the $\kappa$ values of $\beta$-CD itself at the same concentrations.

**Preparation of Solution Samples for Evaluating the Effect of MII on MLCI.** The concentrations of the ligands ($Na_2H_2EDTA$ and its three analogs) as well as $CuCl_2$ in mixed solutions were kept constant (5.00 × $10^{-4}$ mol·dm$^{-3}$). The mixed solutions were detected at 298 K by UV−vis spectroscopy in the case of without and with $\beta$-CD (5.00 × $10^{-4}$ mol·dm$^{-3}$) to confirm effects of MII on MLCI.

Furthermore, to make direct comparisons of the effects, a series of solutions were prepared and analyzed. In each case, the total concentrations of $\beta$-CD (8.33, 7.14, 6.25, and 5.56 × $10^{-4}$ mol·dm$^{-3}$) and the coordination compounds (1.67, 2.86, 3.75, and 4.44 × $10^{-4}$ mol·dm$^{-3}$) formed by the ligands and $CuCl_2$ were kept constant at 1.00 × $10^{-3}$ mol·dm$^{-3}$.

**Preparation of Solution Samples for Studying Concentration Dependences.** Aqueous solutions of 2.00 × $10^{-4}$ mol·dm$^{-3}$ of $Na_2H_2EDTA$ and $CuCl_2$ in the presence of different concentrations of $\beta$-CD (from 0.00 to 50.00 × $10^{-4}$ mol·dm$^{-3}$) were prepared and analyzed by UV−vis spectroscopy. All solutions were prepared in deionized distilled water and stirred for 10 min at 298 K before measurements.

The stability constants ($K_s$) of the complexes between $\beta$-CD and the $[Cu(EDTA)]^{2-}$ formed by $CuCl_2$ with different ligands, $H_4EDTA$, $Na_2H_2EDTA$, $Na_3HEDTA$ and $Na_4EDTA$, were determined by a double-reciprocal plot of absorbance against $\beta$-CD concentration using the following equation.[23]

$$\frac{1}{A_{\max} - A_0} = \frac{1}{a} + \frac{1}{aK_sC_0} \tag{1}$$

In this equation, $A_{\max}$ and $A_0$ represent the absorbance values of the $[Cu(EDTA)]^{2-}$ with and without $\beta$-CD at the maximum absorbance wavelength, respectively, and letting $A_{\max} - A_0 = \Delta A_{\max}$. The $a$ is a constant reflecting the difference between the molar extinction coefficients of the $[Cu(EDTA)]^{2-}-\beta$-CD and $[Cu(EDTA)]^{2-}$ at the same wavelength, and $C_0$ is the initial concentration of $\beta$-CD in a solution. The initial concentrations of $CuCl_2$ and the ligands are kept constant at 2.00 × $10^{-4}$ mol·dm$^{-3}$, while the concentration of $\beta$-CD varies in the range from 0.00 to 50.00 × $10^{-4}$ mol·dm$^{-3}$.

**Instruments and Methods.** Elemental analyses were carried out on an Elementar Vario EL III elemental analyzer. The sodium content in the $Na_2H_2EDTA-\beta$-CD was determined by flame atomic absorption spectrometry (FAAS) using a PerkinElmer AAnalyst 800 (PerkinElmer, U.S.A.). The results of elemental analyses: $Na_2H_2EDTA-\beta$-CD, Anal. Calcd for $C_{52}H_{84}N_2Na_2O_{43}\cdot 4H_2O$: C, 40.43; H, 5.96; N, 1.81; Na, 2.98. Found: C, 40.38; H, 6.05; N, 1.83; Na, 2.89. Therefore, the complexation stoichiometry of $\beta$-CD and

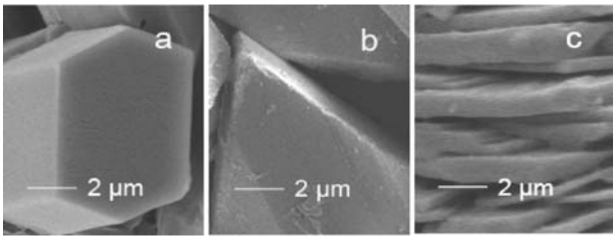

**Figure 2.** FE-SEM images of (a) $\beta$-CD, (b) $Na_2H_2EDTA$, and (c) $Na_2H_2EDTA-\beta$-CD.

$Na_2H_2EDTA$ in the solid complex is one-to-one. The water content present in the complex (about 4 mols per formula unit) is in good agreement with TG analysis (4.09).

$^1H$ nuclear magnetic resonance ($^1H$ NMR) data of $\beta$-CD and $Na_2H_2EDTA-\beta$-CD in $D_2O$ were obtained on a Bruker NMR spectrometer at 300 MHz using $CDCl_3$ with 0.03% v/v TMS as an external reference at 298 K. $^1H$ NMR (300 MHz, $D_2O$, 298 K) of $\beta$-CD: $\delta$ 5.085 (d, 7H, $J$ = 3.7 Hz, $C_1H$ of $\beta$-CD), 3.965 (t, 7H, $J$ = 9.5, $C_3H$ of $\beta$-CD), 3.893 (s, 7H, $C_6H$ of $\beta$-CD), 3.855 (s, 7H, $C_5H$ of $\beta$-CD), 3.680 (d, 7H, $J$ = 3.7, $C_2H$ of $\beta$-CD), 3.594 (d, 7H, $J$ = 9.0, $C_4H$ of $\beta$-CD). $^1H$ NMR (300 MHz, $D_2O$, 298 K) of $Na_2H_2EDTA-\beta$-CD: $\delta$ 5.055 (d, 7H, $J$ = 3.5 Hz, $C_1H$ of $\beta$-CD), 3.946 (t, 7H, $J$ = 9.5, $C_3H$ of $\beta$-CD), 3.874 (d, 7H, $J$ = 4.3, $C_6H$ of $\beta$-CD), 3.830 (s,7H, $C_5H$ of $\beta$-CD), 3.616 (t, 7H, $J$ = 3.7, $C_2H$ of $\beta$-CD), 3.551 (d, 7H, $J$ = 9.2, $C_4H$ of $\beta$-CD).

$^1H$ NMR titration measurements were operated by addition of the solutions of $Na_2H_2EDTA$ ranging from 0.00 to $5.00 \times 10^{-2}$ mol·dm$^{-3}$ to a solution of $\beta$-CD ($1.0 \times 10^{-3}$ mol·dm$^{-3}$) at 298 K using $D_2O$ as solvent. The chemical shifts of protons of $\beta$-CD were recorded on a Bruker NMR spectrometer at 300 MHz using $CDCl_3$ with 0.03% v/v TMS as an external reference. All the sample solutions before use were stirred for 3 h at room temperature under ultrasonic vibration.

The two-dimensional rotating frame nuclear Overhauser effect spectroscopy (ROESY) experiments were performed on a Bruker AV400 (400 MHz) spectrometer with $D_2O$ as solvent using a mixing time of 200 ms. A Bruker standard sequence was applied to make an observation of an intermolecular nuclear Overhauser effect (NOE) between $\beta$-CD and $H_2EDTA^{2-}$ or between $\beta$-CD and $[Cu(EDTA)]^{2-}$.

Crystal morphologies were observed using a Supra 40 field-emission scanning electron microscopy (FE-SEM) operated at 5 kV. X-ray diffraction (XRD) patterns of solid samples were recorded in a Philips X'Pert Pro X-ray diffractometer. Samples were irradiated with monochromatized Cu Kα and analyzed with $5° \leq 2\theta \leq 45°$. Tube voltage and current were 40 kV and 40 mA, respectively.

Thermogravimetry (TG) analyses were performed on a Shimadzu TGA-50 thermogravimetric analyzer at a constant heating rate of 10 K min$^{-1}$ under a nitrogen atmosphere with a gas flow of 25 mL min$^{-1}$. Gas chromatography coupled to time-of-flight mass spectrometry (GC-TOF-MS) measurements with a programmed temperature operation were carried out with a Micromass GCT-MS spectrometer using a standard direct insertion probe for samples.[24]

The $\kappa$ values of solutions were measured using a Leici DDSJ-308 conductivity meter (Shanghai Leici Instrument factory, China) with automatic temperature compensation at 298 K and automatic calibration. A conductance cell with a cell constant of around 0.984 cm$^{-1}$ was used in a water bath whose temperature was kept at 298 K. The $\kappa$ values for comparison were an average of three independent experiments.

UV−vis absorption spectra were taken on a TU-1901 spectrophotometer over the wavelength range from 190 to 600 nm, using quartz cells with a 1 cm optical path at room temperature. The pH values of solutions were determined by a pHS-3C digital pH-meter (Shanghai Jinmai Experimental Instrument Factory, Shanghai, China) equipped with a combined glass−calomel electrode.

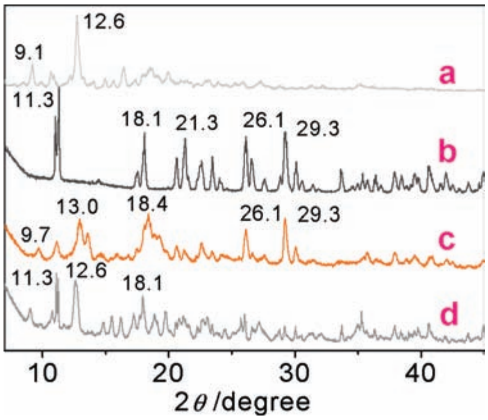

**Figure 3.** XRD patterns of (a) $\beta$-CD, (b) $Na_2H_2EDTA$, (c) $Na_2H_2EDTA-\beta$-CD, and (d) the physical mixture of $\beta$-CD and $Na_2H_2EDTA$ with a molar ratio of 1:1.

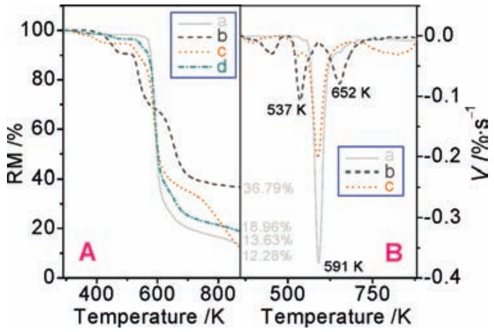

**Figure 4.** (A) TG and (B) DTG profiles of (a) $\beta$-CD, (b) $Na_2H_2EDTA$, (c) $Na_2H_2EDTA$-$\beta$-CD, and (d) the fitted theoretical curve based on a mixed form of $\beta$-CD and $Na_2H_2EDTA$ with a molar ratio of 1:1.

## RESULTS AND DISCUSSION

**Existence of MII between $Na_2H_2EDTA$ and $\beta$-CD.** *1). Microstructural Analysis.* As shown in panels (a) and (b) of Figure 2, the morphologies of $\beta$-CD and $Na_2H_2EDTA$ present a regular hexagonal prism and a stone-shaped configuration, respectively. Nevertheless, the surface structure of $Na_2H_2EDTA-\beta$-CD is a self-assembled, well-ordered multilayered structure comprising a limited number of uniform layers of approximately the same thickness (1−2 $\mu$m) embedded in one crystal. Such a phenomenon also appears in the case of $H_4EDTA$, but each layer is thinner (<1 $\mu$m).[25] This change in morphologies is a result of anisotropy of growth rates, which gives an impression that the crystallization process of the mixed ingredients is regulated by the MII between the ingredients.

The drastic change in crystal morphologies prompts us to examine whether the MII would result in a substantial change in crystal structures. Figure 3 illustrates the XRD patterns of a group of samples that have been tested in parallel. Obviously, the MII leads to a shift or disappearance of characteristic signals of $\beta$-CD (monoclinic) at 9.1° (101) and 12.6° (111) and $Na_2H_2EDTA$ (orthorhombic) at 11.3° (020), 18.1° (002) and 21.3° (231), suggesting a change in stacking sequence. This gives a clear indication of the importance of MII effects. However, such a situation does not occur in the case of the physical mixture (Figure 3d). Furthermore, free $Na_2H_2EDTA$ shows strong peaks at higher $2\theta$ angles such as at 26.1° (430) and 29.3° (422). The

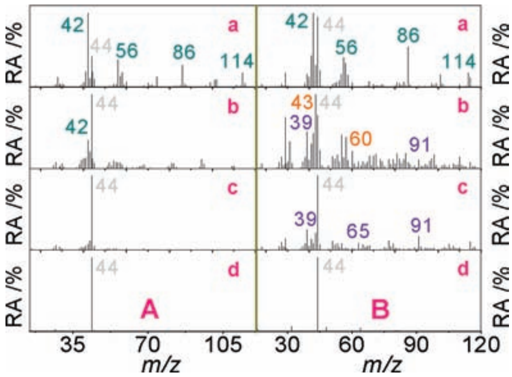

**Figure 5.** Mass spectra of (A) $Na_2H_2EDTA$ and (B) $Na_2H_2EDTA-\beta$-CD at (a) 17.40, (b) 25.34, (c) 31.60, and (d) 36.94 min.

two peaks nearly disappear in the physical mixture but still appear in $Na_2H_2EDTA-\beta$-CD. Therefore, a comparison of the mixing efficiencies obtained from the experimental results provides meaningful insight into understanding the different mixing behaviors of an organic molecule and an organic salt.

*2). Decomposition Process Analysis.* In order to examine the influence of MII on the thermal stability of mixed components, TG measurements of a group samples under entirely identical experimental conditions are performed. As shown panel (A) of in Figure 4, the final residual mass (RM, %) of $Na_2H_2EDTA-\beta$-CD is 12.28% at 870 K. This is lower than that of either of the two free components: $\beta$-CD (RM, 13.63%) and $Na_2H_2EDTA$ (36.79%). Further, the fitted theoretical curve based on a mixed form of $\beta$-CD and $Na_2H_2EDTA$ in a 1:1 molar ratio indicates a RM value of 18.96% at the same temperature. In the light of calculation, the theoretical RM values of $Na_2H_2EDTA$ and $\beta$-CD at 870 K are 8.42 and 10.54%, respectively, if there is no interaction between them. These comparisons not only imply that the $Na_2H_2EDTA-\beta$-CD is not a simple physical mixture, particularly when associated with changes in microstructures, but also exhibit that such a mixing behavior makes a remarkable acceleration effect on the decomposition of the mixed components at a higher temperature.

Additionally, the profiles of derivative thermogravimetry (DTG) in panel (B) of Figure 4 show that $Na_2H_2EDTA-\beta$-CD gives an about 46% decrease in the maximum decomposition rate ($V_m$, $-0.202\%\cdot s^{-1}$), when compared to pure $\beta$-CD ($-0.375\% s^{-1}$), and an increase in decomposition rates ($V$) at a higher temperature range from 718 to 870 K. Similar results are obtained when the analogs of $Na_2H_2EDTA$ are used.[25]

The change in decomposition processes of the interacted components is verified by comparing results from sintering experiments of the samples.[25] Together, these results create a strong impression that the MII between $Na_2H_2EDTA$ and $\beta$-CD produces a large change, including a decrease of RM and an increase in $V$ at higher temperatures.

*3). Decomposition Product Analysis.* Figure 5 shows the mass spectra of $Na_2H_2EDTA$ and $Na_2H_2EDTA-\beta$-CD at several different heating times. A comparison on the same time scale provides indications as to what is the effect of such a MII on the relative abundance (RA, %) of decomposition products.

On the one hand, several interesting fragments: $m/z$ 42.034 ($C_2H_4N^+$, RA, 100.0%), 56.050 ($C_3H_6N^+$, 36.71%), especially 86.060 ($C_2H_6N_4^+$, 2-azidoethanamine, 30.05%) and 114.056 ($C_2H_6N_6^+$, 3,4,5-triamino-1,2,4-triazole, 19.38%) occur at a lower temperature (553 K, 17.40 min), which are all associated with C−N bond cleavages of $Na_2H_2EDTA$, and the RA value of 2-azidoethanamine is increased to 54.29% in the presence of $\beta$-CD. Moreover, as the temperature rises to 653 K (25.34 min), the $Na_2H_2EDTA-\beta$-CD exhibits a very strong signal of $m/z$ 43.018 ($N_3H^+$, hydrogen azide, 100.0%), but the RA value of the signal is 21.05% in the case of free $Na_2H_2EDTA$. It is important to note that $Na_2H_2EDTA$ decomposes to generate azide radicals in high abundance.

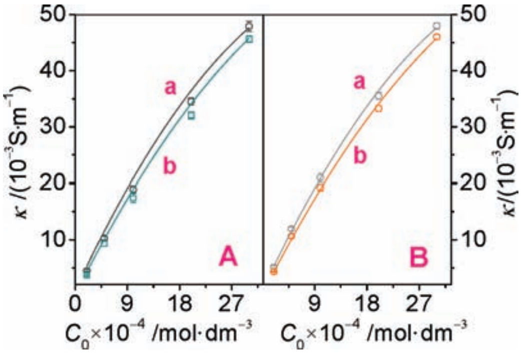

**Figure 6.** Plots of $\kappa$ versus the initial concentrations ($C_0$) of (A) $Na_2H_2EDTA$ and (B) $CuCl_2$ in the absence (a) and presence (b) of $\beta$-CD. Typical error bars are shown in the figure. The $C_0$ values of components in mixed solutions are the same.

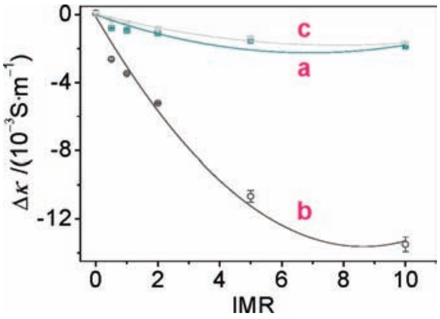

**Figure 7.** $\Delta\kappa$ as a function of the initial molar ratios (IMR) of $\beta$-CD (from 0.00 to $1.00 \times 10^{-2}$ mol$\cdot$dm$^{-3}$) to (a) $Na_2H_2EDTA$ ($1.00 \times 10^{-3}$ mol$\cdot$dm$^{-3}$), (b) $CuCl_2$ ($1.00 \times 10^{-3}$ mol$\cdot$dm$^{-3}$), and (c) their mixed solutions (1:1, molar ratio).

On the other hand, the decomposition behavior of $\beta$-CD is also affected largely. For instance, the two strongest peaks of free $\beta$-CD at $m/z$ 60.020 ($C_2H_4O_2^+$, 97.62%) and 73.029 ($C_3H_5O_2^+$, 100.0%)[24] are significantly weakened by the presence of $Na_2H_2EDTA$. In addition, a group of tropylium ions: $m/z$ 39.023 ($C_3H_3^+$, 27.35%), 65.039 ($C_5H_5^+$, 7.02%), and 91.053 ($C_7H_7^+$, 18.58%) have markedly higher RA values than those in the cases of $\beta$-CD and $Li_2CO_3$-$\beta$-CD.[26]

These results point toward the existence of MII between $Na_2H_2EDTA$ and $\beta$-CD and provide an experimental ground for further attempts to apply the MII for enhancement or suppression of chemical reactivities of molecules or ions. To test this idea, efforts were made to give evidence of the presence of MII in solutions and explore the relationship between MII and MLCI.

**Evidence of the Presence of MII in Solutions.** Figure 6 depicts the effect of $\beta$-CD on the $\kappa$ values of aqueous solutions of $Na_2H_2EDTA$ as well as $CuCl_2$ at different concentrations at 298 K. In each case, the concentrations of both the salts and $\beta$-CD in mixed solutions are taken to be equal. Clearly, addition of $\beta$-CD to the solutions leads to a decrease of $\kappa$, and the decrease ($\Delta\kappa$) indicates a

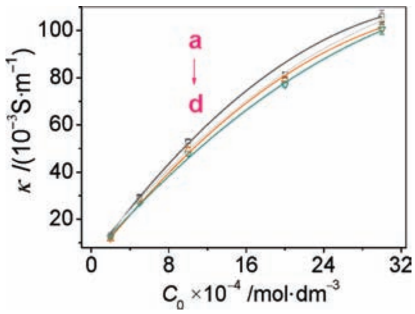

**Figure 8.** Plots of $\kappa$ against $C_0$ values of components in mixed solutions using the following addition orders: (a) $Na_2H_2EDTA + CuCl_2$, (b) $S_1$: $Na_2H_2EDTA + CuCl_2 + \beta$-CD, (c) $S_2$: $Na_2H_2EDTA + \beta$-CD + $CuCl_2$, and (d) $S_3$: $CuCl_2 + \beta$-CD + $Na_2H_2EDTA$. At each point, the $C_0$ value of mixed components in solutions is the same.

tendency toward an increasing level with increasing total concentration of the mixed components. Furthermore, both $Na_2H_2EDTA$ and $CuCl_2$ at the same concentrations present a similar response for the introduction of $\beta$-CD and its concentration in solutions. These observations provide important information concerning the existence and extent of the interactions between $Na_2H_2EDTA$ and $\beta$-CD and between $CuCl_2$ and $\beta$-CD.

Figure 7 displays the relationships between concentrations of $\beta$-CD and $\Delta\kappa$ values of solutions of $Na_2H_2EDTA$, $CuCl_2$, and their coordination compound. The $\Delta\kappa$ values exhibit a decreasing trend with the addition of $\beta$-CD. The decrease in ion mobility is ascribed to interactions of ions with the end hydroxyl groups of $\beta$-CD.[27−29]

Apparently, the effect of increasing concentrations of $\beta$-CD produces a small and nearly equivalent response for $Na_2H_2EDTA$ and the coordination compound but presents a large and different behavior response to $CuCl_2$. There are two possible interpretations for this finding. The first possibility is that the $\beta$-CD-induced block for ion mobility, in which case, larger ions such as $H_2EDTA^{2-}$ and $[Cu(EDTA)]^{2-}$ should be far more restricted by the blocking behavior. This is contrary to the result observed in Figure 7. The other possibility is that small ions such as $Cu^{2+}$ and $Cl^-$ have more opportunities to be trapped by the surface hydroxyl groups of $\beta$-CD molecules. This assumption is in agreement with the experimental data. These observations reflect a similar mechanism of action between $Na_2H_2EDTA$ and its coordination compound, implying that the effect of $\beta$-CD on the coordination compound is mainly reflected by its impact on $Na_2H_2EDTA$. Also, the same effects are observed in the cases of the analogs of $Na_2H_2EDTA$ when the concentration of $\beta$-CD is increased.[25] These results provide a dramatic demonstration that the MII is responsible for the decrease in ion mobility in salt solutions.

Also, it is possible that the MII may exert an influence on the coordination process of $Na_2H_2EDTA$ and $CuCl_2$. It is thus of considerable interest to study the mutual effect between MII and MLCI in a multicomponent system. Figure 8 gives the results of such an investigation. Through comparison, we see that the coordination abilities of $Na_2H_2EDTA$ and $CuCl_2$ are indeed influenced by addition of $\beta$-CD, regardless of the change in addition orders. Besides, as shown in Figures 7 and 8, the extent of influence is under the control of addition orders of salts. The fact that different addition orders of reagents have different effects reveals that there may be a competitive effect of MII on MLCI. In order to support this argument, we furnish a new proof showing the link between the two interactions.

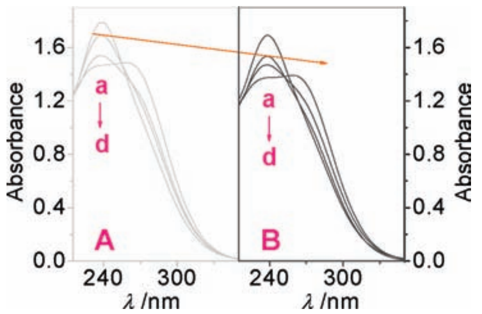

**Figure 9.** UV−vis spectra of $[Cu(EDTA)]^{2-}$ formed by $CuCl_2$ ($5.00 \times 10^{-4}$ mol·dm$^{-3}$) with (a) $H_4EDTA$, (b) $Na_2H_2EDTA$, (c) $Na_3HEDTA$, and (d) $Na_4EDTA$ ($5.00 \times 10^{-4}$ mol·dm$^{-3}$) in the absence (A) and presence (B, $5.00 \times 10^{-4}$ mol·dm$^{-3}$) of $\beta$-CD.

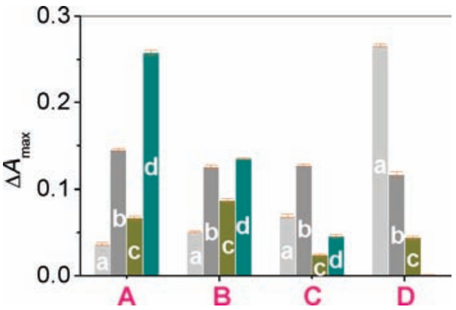

**Figure 10.** Decrease in $A_{max}$ of $[Cu(EDTA)]^{2-}$ at 238 nm caused by addition of $\beta$-CD. The concentrations of $[Cu(EDTA)]^{2-}$ and $\beta$-CD are (A) 1.67 and 8.33, (B) 2.86 and 7.14, (C) 3.75 and 6.25, and (D) 4.44 and $5.56 \times 10^{-4}$ mol·dm$^{-3}$, respectively. $[Cu(EDTA)]^{2-}$ is formed by $CuCl_2$ with (a) $H_4EDTA$, (b) $Na_2H_2EDTA$, (c) $Na_3HEDTA$, and (d) $Na_4EDTA$.

**Competitive Relationship between MII and MLCI.** Figure 9 depicts the UV−vis absorbance curves of the coordination compound ($[Cu(EDTA)]^{2-}$) formed by $CuCl_2$ with $Na_2H_2EDTA$ in the absence and presence of $\beta$-CD. No absorbance is observed in this region for the free components. Evidently, the addition of $\beta$-CD causes a decrease in the maximum absorbance ($A_{max}$) of $[Cu(EDTA)]^{2-}$ at 238 nm, signifying that $\beta$-CD plays a negative role in the regulation of the MLCI between $CuCl_2$ and $Na_2H_2EDTA$, as shown by an arrow in Figure 9. Similar decreases ($\Delta A_{max}$) are shown in several analogs of $Na_2H_2EDTA$ as well. These results give a clear hint that the presence of $\beta$-CD makes an influence on the MLCI. The influence is explained as the existence of a competitive relationship between MII and MLCI.

The bar diagrams shown in Figure 10 further describe the influence of different concentrations of $\beta$-CD on the magnitude of $A_{max}$ in the coordination compounds with the same initial concentrations.

As shown in Figure 10, $Na_2H_2EDTA$ system has a moderate and almost uniform response to the decrease in concentration differences between $\beta$-CD and $[Cu(EDTA)]^{2-}$. Interestingly, the $\Delta A_{max}$ values gradually increase from $H_4EDTA$, $Na_2H_2EDTA$ to $Na_4EDTA$ in the case of a large concentration difference such as $6.66 \times 10^{-4}$ mol·dm$^{-3}$. By contrast, there is a clear downward trend in $\Delta A_{max}$ from $H_4EDTA$, $Na_2H_2EDTA$, $Na_3HEDTA$ to $Na_4EDTA$ when a small concentration difference ($1.12 \times 10^{-4}$ mol·dm$^{-3}$) occurs.

These findings indicate that the competitive relationship between MII and MLCI is associated with the concentration

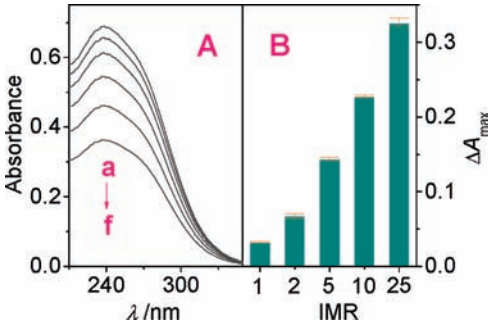

**Figure 11.** (A) UV−vis spectra of $[Cu(EDTA)]^{2-}$ formed by $2.00 \times 10^{-4}$ mol·dm$^{-3}$ $CuCl_2$ with $2.00 \times 10^{-4}$ mol·dm$^{-3}$ $Na_2H_2EDTA$ in the presence of β-CD. The concentrations of β-CD from curves a to f are 0.00, 2.00, 4.00, 10.00, 20.00, and $50.00 \times 10^{-4}$ mol·dm$^{-3}$. (B) $\Delta A_{max}$ of $[Cu(EDTA)]^{2-}$ ($2.00 \times 10^{-4}$ mol·dm$^{-3}$) at 238 nm as a function of the IMR of β-CD to $[Cu(EDTA)]^{2-}$.

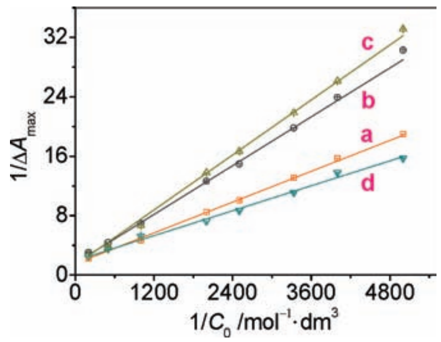

**Figure 12.** Plots of $1/\Delta A_{max}$ versus $1/C_0$ in the systems of $2.00 \times 10^{-4}$ mol·dm$^{-3}$ $CuCl_2$ with $2.00 \times 10^{-4}$ mol·dm$^{-3}$ (a) $H_4EDTA$, (b) $Na_2H_2EDTA$, (c) $Na_3HEDTA$, and (d) $Na_4EDTA$ in the presence of β-CD ($C_0$, 0.00−$50.00 \times 10^{-4}$ mol·dm$^{-3}$).

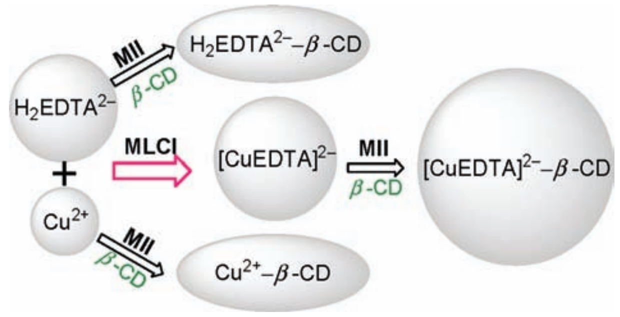

**Figure 13.** Schematic sketch illustrating the proposed competitive relationship between MII and MLCI.

difference between β-CD and the coordination compounds of $CuCl_2$, and different coordination systems exhibit a completely different response to changes in concentration differences. It should be noted that both pH and ionic strength are different in the parallel multicomponent systems, though all the coordination ions formed in solutions are the same ($[Cu(EDTA)]^{2-}$).[25] This is possibly one reason why there is variability in $Na_2H_2EDTA$ and its analogs.

**Concentration Dependence of the Effect of β-CD on MLCI.** Figure 11 illustrates the correlation between the absorbance of $[Cu(EDTA)]^{2-}$ and the concentration of β-CD. An increasingly negative effect imposed by the increasing concentration of β-CD on the MLCI between $CuCl_2$ and $Na_2H_2EDTA$ is shown in panel (A) of Figure 11. The extent of the negative effect is depicted in bar diagrams (Figure 11B).

The gradual decrease in $A_{max}$ values clearly demonstrates that the MLCI between $CuCl_2$ and $Na_2H_2EDTA$ is weakened by increasing concentrations of β-CD, indicating the involvement of the MII between β-CD and the two coordination components. This involvement is likely to result in a decrease in effective concentration of the coordination components. The extent of this weakening phenomenon is apparently dependent on the concentration of β-CD, signifying that there is a concentration dependence of the effect of β-CD on the MLCI. In a word, when several interactions exist simultaneously in a multicomponent system, a weak interaction such as MII may make a negative contribution to a strong interaction such as MLCI.

Figure 12 shows the double-reciprocal plots of $1/\Delta A_{max}$ versus $1/C_0$. The $C_0$ values of $CuCl_2$ and the ligands are kept at $2.00 \times 10^{-4}$ mol·dm$^{-3}$, while the concentration of β-CD varies in the range from 0.00 to $50.00 \times 10^{-4}$ mol·dm$^{-3}$. As shown in the figure, the fits to the data points are satisfactory, with the correlation coefficients of more than 0.990. The $K_s$ values of the complexes between β-CD and the $[Cu(EDTA)]^{2-}$ formed by $CuCl_2$ with different ligands, $H_4EDTA$, $Na_2H_2EDTA$, $Na_3HEDTA$ and $Na_4EDTA$, are determined to be 440.5, 289.6, 220.4, and 697.9 mol$^{-1}$·dm$^3$ , respectively, by means of slopes and intercepts of the linear plots (Figure 12) on the basis of eq 1 described in the Experimental Section. For the four interaction systems, the good linear correlations in the investigated concentration range probably suggest that the stoichiometries of the complexes in solutions are 1:1.

The calculated $K_s$ values reveal two aspects of special interest. First, there is a considerable interaction between β-CD and the $[Cu(EDTA)]^{2-}$, and the level of interaction intensity is comparable to those observed in numerous other β-CD complexes of hydrophobic guests.[30] Second, the large difference between $K_s$ values reflects that this interaction between the β-CD and the coordination ion $[Cu(EDTA)]^{2-}$ is related to the nature of the ligands because the ligands have different affinities to the $Cu^{2+}$ ions in the presence of β-CD (Figure 10).

Figure 13 provides a schematic representation of the competitive relationship between the two types of interactions. On the one hand, the MLCI between $H_2EDTA^{2-}$ and $Cu^{2+}$ ions leads to the formation of $[Cu(EDTA)]^{2-}$ in solution. On the other hand, the MII between β-CD molecules and the ions like $Cu^{2+}$, $H_2EDTA^{2-}$ and $[Cu(EDTA)]^{2-}$ can be understood as follows. The large number of hydroxyl groups present in β-CD molecules makes them interact strongly with the cations such as $Cu^{2+}$ and $Na^+$ ions, and the large anions such as $H_2EDTA^{2-}$ and $[Cu(EDTA)]^{2-}$ are more apt to interact with the hydrogen atoms of glycosidic bonds of β-CD. Undoubtedly, structural information on the interaction mode between β-CD and the ions is crucial for gaining deeper insights into the nature of the interaction.

Earlier reports give information on determining the complexation interaction sites of β-CD and organic guests by $^1H$ NMR measurements.[31−34] This urges us to investigate the interaction mechanism between $Na_2H_2EDTA$ and β-CD.

Figure 14 shows the result of $^1H$ NMR titration measurements for β-CD before and after interaction with $Na_2H_2EDTA$. Actually, the existence of the MII between them is clearly confirmed by the comparison between the curves obtained at different

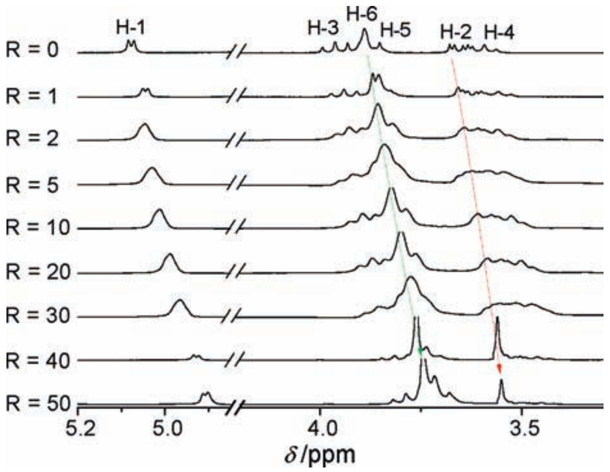

**Figure 14.** Chemical shifts (δ, ppm) of the protons of β-CD at different concentration ratios ($R$ = 0−50) of $Na_2H_2EDTA$ to β-CD in $D_2O$.

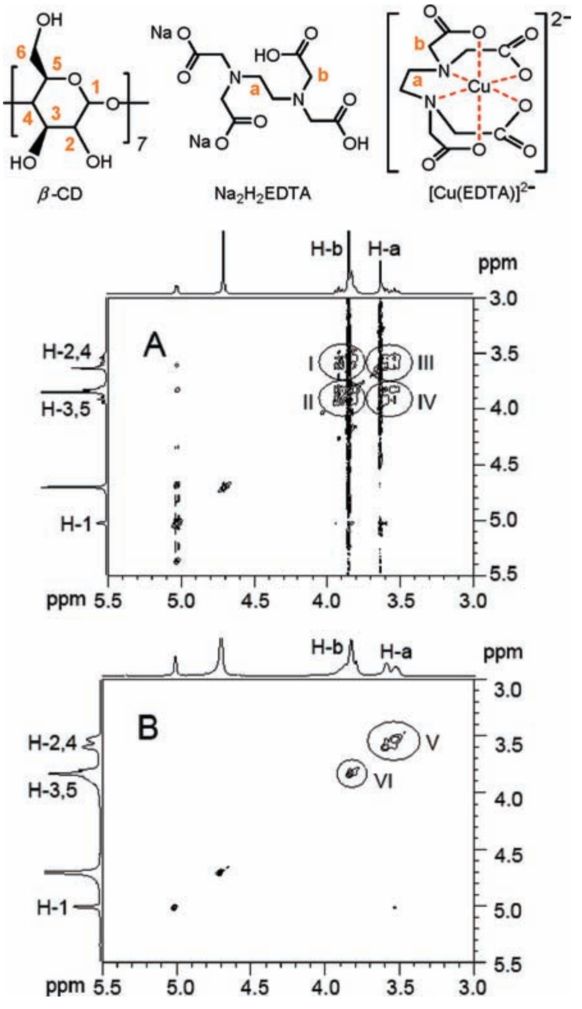

**Figure 15.** ROESY spectra of (A) $Na_2H_2EDTA$−β-CD and (B) $[Cu(EDTA)]^{2-}$−β-CD in $D_2O$ at 300 K.

concentration ratios ($R$) of $Na_2H_2EDTA$ to β-CD. As shown by the arrow directions, the MII leads to an upfield shift of proton signals on all the carbon atoms in β-CD molecules. Such an upfield shift is due to an increase in the electron density in the hydrogen atoms of glycosidic bonds of β-CD after interaction with the $H_2EDTA^{2-}$.

Furthermore, the magnitude of the upfield shift of the proton signals increases with an increase in $R$ values, implying the dependence of the MII between β-CD and $Na_2H_2EDTA$ on the concentration of the interacting ion $H_2EDTA^{2-}$. In our opinion, the concentration dependences displayed in Figures 11 and 14 are very important for the understanding of the effect of the MII on the MLCI between $H_2EDTA^{2-}$ and $Cu^{2+}$. For example, the result of Figure 14 could be one reason for the phenomenon observed in Figure 11. As a consequence, the different concentration dependences in the behavioral profile of the ternary system give an impression that the competitive relationship between the MII and the MLCI may be mediated by the regulation of the concentrations of the host and the ligand in solutions.

In addition, as shown in Figure 14, the protons inside (H-3 and H-5) and outside (H-2 and H-4) of the β-CD cavity shift simultaneously, but the latter shows a smaller shift with increasing $R$ values. This means that the $H_2EDTA^{2-}$ in higher concentrations prefers to enter the β-CD cavity.

Panel (A) of Figure 15 shows that there are four obvious cross-peaks (I−IV) associated with the MII between the protons of $Na_2H_2EDTA$ and β-CD. Clearly, the NOE cross-peaks (IV and II) between H-3/H-5 protons of β-CD and H-a/H-b protons of the anion $H_2EDTA^{2-}$ indicate that one part of the anion is included into the β-CD cavity. Also, the NOE cross-peaks between the H-a/H-b protons and H-2/H-4 protons of β-CD are observed (III and I), suggesting that the other part of the anion has an interaction with the outside-cavity protons of β-CD. Moreover, the similar peak intensity of the two parts shows that the aliphatic carbon chains of the anion have a similar distribution inside and outside the cavity of β-CD. Therefore, we infer that the anion is only partially accommodated inside the β-CD cavity. In our opinion, such a phenomenon is due to the flexible structure of $Na_2H_2EDTA$.[25]

However, only two cross-peaks (V and VI) are found in the case of $[Cu(EDTA)]^{2-}$−β-CD (Figure 15B). In particular, the NOE cross-peak (V) between the H-a protons of the $[Cu(EDTA)]^{2-}$ and the H-2/H-4 protons of β-CD shows a higher intensity than the NOE cross-peak (VI) between the H-b protons of the $[Cu(EDTA)]^{2-}$ and the H-3/H-5 protons of β-CD. These results reveal that the interaction between β-CD and the $[Cu(EDTA)]^{2-}$ occurs mainly on the outer surface of the cavity wall of β-CD. This is probably because the $[Cu(EDTA)]^{2-}$ has a rigid structure, resulting in only partial insertion into the cavity.[25]

## ■ CONCLUSIONS

In this study, we first examined the presence of MII between $Na_2H_2EDTA$ and β-CD by displaying the difference in microstructures and the change in thermal decomposition processes and products before and after interaction. Next, electric conductivity measurements provided strong evidence for supporting the existence of the MII between $Na_2H_2EDTA$ and β-CD, as well as between $CuCl_2$ and β-CD, and then, a competitive relationship between MII and MLCI was proposed to explain the decrease phenomenon observed in the maximum absorbance of the coordination compound formed by $Na_2H_2EDTA$ and $CuCl_2$. Moreover, we found that there is a concentration dependence of the effect of β-CD on the MLCI. Finally, the result of $^1H$ NMR measurements exhibited that there were different interaction modes of $\beta$-CD with $H_2EDTA^{2-}$ and $[Cu(EDTA)]^{2-}$. We believe that the present work would be useful to understand the mutual influence between several kinds of interactions in multicomponent systems.

## ■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** (1) Heating program in GC-TOF-MS experiments; (2) TG/DTG profiles of $\beta$-CD, $Na_2H_2E$-DTA analogs ,and their interacted products; (3) FE-SEM images of $Na_2H_2EDTA$ analogs; (4) data from sintering experiments of $\beta$-CD, the ligands, and their interacted products; (5) UV—vis spectra of coordination compounds formed by $CuCl_2$ and $Na_2H_2EDTA$ analogs in the absence and presence of $\beta$-CD; and (6) proposed interaction modes of $\beta$-CD with $H_2EDTA^{2-}$ and $[Cu(EDTA)]^{2-}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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