



Thermal release behavior of Fe^+ , CpFe^+ and $(\text{Cp})_2\text{Fe}^+$ ions from the molecular aggregate of β -cyclodextrin with ferrocene

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ABSTRACT

The second-sphere interactions between ferrocene (Fc, guest) analogs and cyclodextrins (CD, host) have attracted sufficient attention in the past decades. However, there are some unanswered questions related with the interactions. For example, how such interactions are reflected by the thermal decomposition process? The present report describes our efforts to elucidate the correlation between the destruction of a second-sphere complex through the release of its members and the separate destruction of its members by a direct sample introduction device with programmed temperature in a gas chromatography coupled to time-of-flight mass spectrometry. Different kinds of mass spectra are analyzed to elicit accurate details about sample decomposition processes. It is found that on the one hand, the presence of Fc effectively delays the decomposition temperature of the complexed β -CD though a great part of Fc has been released from the complex. On the other hand, the special molecular structure of β -CD has served to prevent the sublimation of Fc to a certain degree. Furthermore, the thermal decomposition mode of the β -CD molecules complexed by Fc is drastically changed compared with that of free β -CD. Also, this study provides a paradigm that ferrocene decomposes in the β -CD cavity through the release of a CpFe^+ moiety, and the remaining Cp ring remains contained in the host.

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1. Introduction

β -Cyclodextrin (β -CD) is composed of seven oligosaccharides, creating a rigid conical molecular structure with a hydrophobic cavity [1,2]. This cavity can accommodate many kinds of guests [3–7] and there are lots of reports about the application of the complexes in improving the properties of organic guests, such as stability, solubility, and controlled-releasing [8,9]. Ferrocene (Fc) is an organometallic compound consisting of two planar and parallel cyclopentadienyl rings and an iron atom. Fc and its various derivatives have been applied in many fields such as synthetic organic chemistry, materials science and catalysis [10–12].

Harada and Takahashi prepared the inclusion complex of β -CD with Fc in 1984 by stirring the mixed aqueous solution of Fc and β -CD [13]. It is the first example on the inclusion phenomenon of β -CD with an organometallic coordination compound. From then on there have been many reports about the second-sphere coordination complexes between derivatives of CDs and organometallic compounds [14–18] accompanying various strategies of characterization [19,20]. Among the characterization techniques, thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses are used most frequently to measure the thermal proper-

ties of the complexes [21–25]. As a matter of course, they can reflect how the mass of samples or the energy of systems changes with the increase of temperature. In recent papers, we found that the thermal decomposition path of β -CD was altered by organic guests included in the cavity of β -CD, and at the same time the decomposition modes of the included guests themselves were also affected because of the inclusion complexation [26]. However, such phenomena were usually submerged during rapid mass loss stages on the TG curves.

Differently from common organic guests, Fc as a coordination complex containing organic ligands, also can interact with β -CD [13]. Although Fc sublimates at about 373 K and the TG curve of its inclusion complex Fc- β -CD presents a continuous mass loss process below 673 K [27], it is difficult to extract the detailed information about the release process of Fc- β -CD from either TG or DSC curve. The information includes: (1) Can the special molecular structure of β -CD prevent the sublimation and decomposition of Fc? (2) What are the configurations of the decomposed products of Fc- β -CD at higher temperature? (3) How Fc behaves during the rapid mass loss stage of β -CD? That is to say, the construction and characterization of a stable supramolecule are important, but at the same time the disruption of it is even more significant, because the disruption is closely related with practical applications that are ignored or underestimated. So far, there are very few reports describing the relationship between the fragment

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composition and the temperature increase of solid supramolecule especially second coordination sphere supramolecule. The present report describes our efforts to elucidate the correlation between the destruction of a second-sphere complex through the release of its members and the separate destruction of its members. A direct sample introduction device with programmed temperature was applied in a gas chromatography coupled to time-of-flight mass spectrometry (GC–TOF–MS). Different kinds of mass spectra were analyzed to elicit more accurate details about sample decomposition processes.

2. Experimental

2.1. Materials

β -CD was purchased from Shanghai Chemical Reagent Company and recrystallized twice from deionized water. Fc was purchased from Shanghai Chemical Reagent Company and used without further purification. All other reagents are of analytical-reagent grade, unless stated otherwise

2.2. Preparation of the inclusion complex Fc– β -CD

The solid complex was prepared with the initial molar ratio of 4:1 (Fc: β -CD) and purified according to the reported method [13]. The host–guest stoichiometric ratio in the solid complex was determined to be 1:1 based on elemental analyses, Anal. Calcd. for $C_{52}H_{80}O_{35}Fe \cdot 3H_2O$: C, 45.38; H, 6.25. Found: C, 45.55; H, 6.34%.

2.3. Measurements

Elemental analyses were carried out on an Elementar Vario EL III elemental analyzer. TG measurements were performed on Shimadzu TGA-50 thermogravimetric analyzer at the heating rate of 10.0 K min^{-1} under a nitrogen atmosphere. GC–TOF–MS experiments were carried out on a Micromass GCT-MS spectrometer using a direct insertion probe for solid samples, with an increasing temperature. Measurement conditions are summarized in Table 1. Three types of diagrams are collected: (1) the variation of total ion current (TIC) as a function of heating time, (2) the variation of ion current for a selected individual as a function of heating time, and (3) mass spectra at specific time points according to the appointed heating program (see Table 1). Computer analysis allows the extraction of fragment signals of interest.

3. Results and discussion

3.1. TG and DTG analyses

Residual mass (RM) and mass loss rate (MLR) as the functions of temperature are presented as TG and differential thermogravimetry (DTG) profiles of Fc– β -CD in Fig. 1. Except for the release of water below 390 K, both of the two curves present obvious mass loss stages in the temperature ranges 393–563 K (Stage A) and

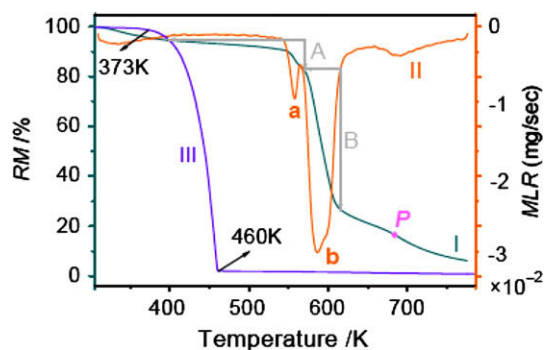


Fig. 1. TG (Curve I), DTG (Curve II) profiles of Fc– β -CD, and TG (Curve III) profile of free Fc.

570–620 K (Stage B), and the fastest mass loss points in Curve II are at 558.7 K (Peak a) for Stage A and 587.1 K (Peak b) for Stage B.

As can be seen, before Stage A in Curve I, there is a stage corresponding to the water release. Furthermore, after Stage B, Fc– β -CD experiences a process of carbonization and incineration. Also, it is interesting that near the center of the process there is an inflection point *p*, after which the release rate changes in response to temperature change. The mass loss of 9.61% in Stage A is apparently lower than the Fc content of 13.53% in the 1:1 inclusion complex Fc– β -CD based on the elemental analysis result. That is to say, the release of some Fc molecules after inclusion has been delayed to the next period, *i.e.*, Stage B. At the same time Curve III displays that the mass loss for free Fc is higher than 98% in the temperature range from 373 to 460 K. From the difference of the release temperature, it is clear that the sublimation and release of the complexed Fc molecules have been protected by the β -CD cavities to a great extent. Also, the decomposition temperature of the complexed β -CD at about 587 K is higher than that of free β -CD [28]. Consequently, it is rather interesting to investigate the protection behavior of β -CD to the sublimation of Fc as well as the influence of the Fc on the complexed β -CD.

3.2. An analysis on the thermal decomposition of free Fc

First of all, the TIC curves for free Fc, β -CD and Fc– β -CD are shown in Fig. 2. The detected ion current signal in Curve B has become the baseline at about 3.10 min, below 313 K according to the temperature program. It means free Fc has been completely gasified at such a low temperature.

Fc sublimates at about 373 K under a general condition. Here the vacuum condition must be the reason for the earlier release

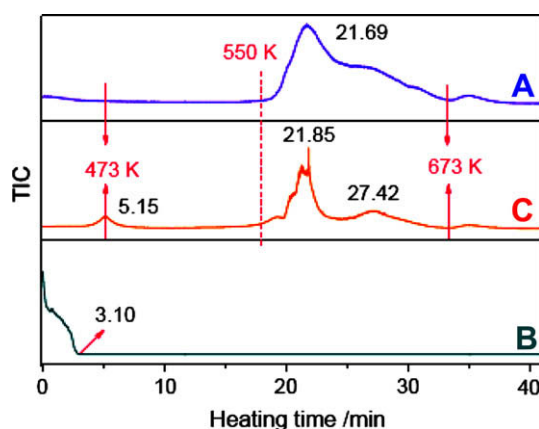


Fig. 2. TIC curves of free β -CD (A), Fc (B) and Fc– β -CD (C).

Table 1
Appointed heating program for the samples.

Step	Temperature range (K)	Heating rate (K min^{-1})	Retained time (min)
1	303	0	3
2	473	80	5
3	673	10	3
4	873	80	10

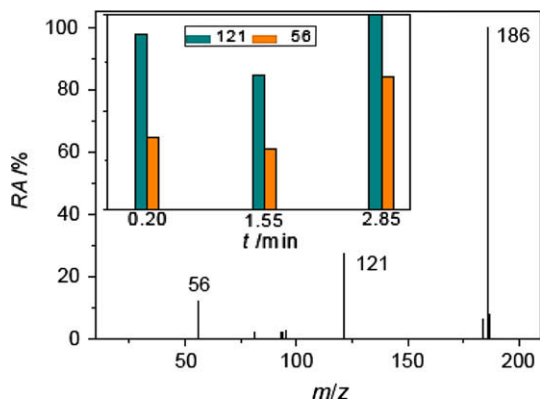


Fig. 3. Mass spectrum of free Fc at 1.55 min and the inset is the RA values of the two major fragments at 0.20, 1.55 and 2.85 min, respectively.

of free Fc. The phenomenon that Fc sublimates completely at lower temperature easily is consistent with the observation of Curve III in Fig. 1.

Next, Fig. 3 illustrates the mass spectrum of free Fc at 1.55 min as well as the relative abundance (RA) change of two main fragments (55.93 and 120.97) at 0.20, 1.55 and 2.85 min.

It is important to note that the mass spectra of free Fc from the beginning to 3.10 min are all very similar to Fig. 3, only showing three major fragment peaks at m/z 186.01 (RA, 100%), 120.97 (13.20%) and 55.93 (40.33%). They correspond to the molecules: $C_{10}H_{10}Fe^+$, $C_5H_5Fe^+$ and Fe^+ , respectively. The signal of m/z 186.01 is the strongest all the time and the RA values of the other two peaks are always lower than 50%. And the change of the absolute values of RA seems to be irregular, but the relative RA values of 120.97–55.93 exhibit a decreased tendency from 2.43 to 1.54. These results not only are in accordance with the stability order of these ions: $C_{10}H_{10}Fe^+ > C_5H_5Fe^+ > Fe^+$, but also suggest that the formation of $C_5H_5Fe^+$ and Fe^+ under GC–MS conditions is feasible.

3.3. An analysis on the graphical tracking curve of complexed Fc

Thermal release behavior of guests from supramolecule is one of the important application fields of host–guest chemistry [29,30], and the release process can also be used to evaluate the intermolecular interactions between host and guest. The significant differences in TIC profiles between free Fc and complexed Fc remind us that the interaction between Fc and β -CD is responsible for the change of the thermal behavior of Fc. Therefore, it is possible that thermal trace curve of the fragment at m/z 186.01 is used to provide a detailed insight into the release behavior of the complexed Fc.

In multiple ion detection mode (MID), the ion current belonging to the complexed Fc in Fc– β -CD is detected, and the relationship between the values of RA and heating time is depicted in Fig. 4.

As seen from Fig. 1, a part of Fc may be released together with the main decomposition process of the complexed β -CD. In Fig. 4, there are three stages for the release process of Fc. The first release stage occurs below 480 K. This is explained by the sublimation of some Fc molecules at lower temperature. Such a kind of Fc is released before the decomposition of β -CD and should have less influence on the thermal behavior of the complexed β -CD.

Continuing to increase the temperature leads to the second release of the remaining Fc in the inclusion complex in the time range from 17 to 21 min, corresponding to the temperature range from 543 to 580 K. Finally, a small quantity of Fc is detected at about 673 K in the third stage. In comparison with the release behavior of free Fc (Fig. 2B), the position of these peaks in MID

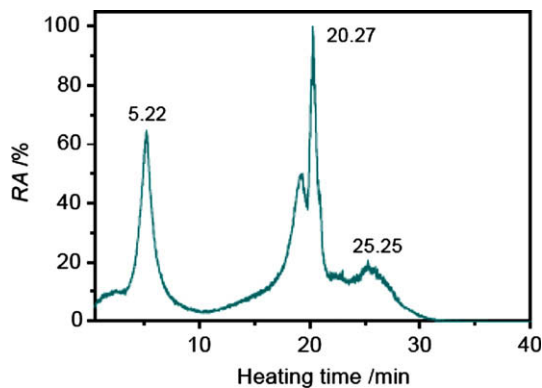


Fig. 4. MID curve of Fc from Fc– β -CD.

curve strongly implies that the thermal release of the complexed Fc is deferred to a great extent. Assuredly, the MID curve of the Fc in the inclusion complex provides a convincing evidence for different release modes of Fc. It should be noted that the observation cannot be seen directly from the TG curves in Fig. 1.

3.4. An analysis on the mass spectrum of complexed Fc at 18.99 min

The decomposition details of the complexed Fc at 18.99 min in our experiments are presented in Fig. 5.

Fig. 5 is a reflection of the main release and decomposition process of the complexed Fc at about 553 K. The fragment of m/z 120.97 is generated after an Fc molecule loses a cyclopentadienyl (Cp) ring. When the two Cp rings in an Fc molecule are lost simultaneously, the fragment of m/z 55.93 is produced. This means that the coordination bonds between Cp rings and Fe atom are broken at the moment.

However, there exists an interesting phenomenon that the fragment signal of the Cp rings (m/z 65.04) possesses a rather lower RA value of 1.06% at the same time. Even if all the possible rupture modes of a Cp ring are taken into consideration, including the smaller fragments of $C_2H_2^+$, $C_3H_3^+$, $C_5H_6^+$ and so on, the total detected RA value does not reach 4%. Combined with the structure of Fc– β -CD [13], it now follows that during the release process of the complexed Fc some Cp rings might continue to be kept in the cavities of β -CD molecules. This phenomenon is ascribed to a strong interaction between the cavity of β -CD and the Cp ring. In our opinion, one of the two Cp rings in this cavity is likely to be surrounded by a plane ring consisting of seven glycosidic oxygen atoms of β -CD, and the van der Waals interaction between the Cp ring and the oxygen atoms may play a significant role in making one Cp ring invulnerable to thermal disturbance, since the interac-

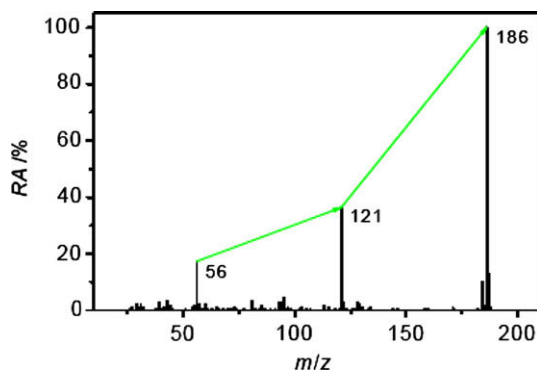


Fig. 5. Mass spectrum of Fc– β -CD at 18.99 min.

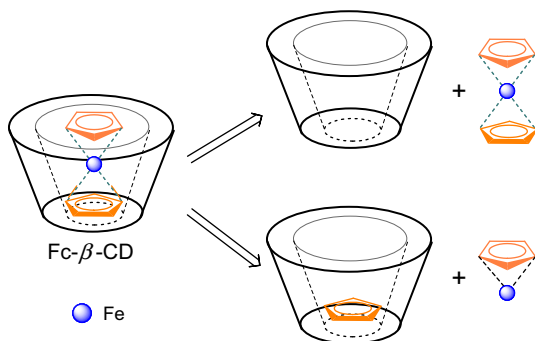


Fig. 6. Two proposed release modes of Fc in Fc- β -CD.

tion does not only make the Cp ring remained in the cavity, but also prevent it from cracking to some extent. The fact that at this temperature the RA values of the characteristic fragments of m/z 60.02 and 43.02 belonging to the cleavage of β -CD skeleton [26] are only 2.37% and 3.18%, respectively, reflects that most of the complexed β -CD molecules are still stable at this moment. Fig. 6 describes two proposed release modes of the bound Fc from its complex of β -CD.

3.5. The difference between the TIC profiles of free β -CD and Fc- β -CD

The plots of TIC versus heating time of free β -CD and Fc- β -CD are shown in Fig. 2. The selected heating rate is 10 K min^{-1} from 473 to 673 K with the aim of investigating the release difference of the two samples during their decomposition process. Actually, large differences are observed between them.

First, there is an obvious small peak at 5.15 min due to the fragment release of Fc in Curve C below 480 K, which does not appear in Curve A.

Subsequently, the initial point of the major peak in Curve C (about 550 K) is lower than that in Curve A (about 560 K). What needs to be pointed out here is that there exists a predecomposition stage in Curve C, forming some fragments with lower RA values. And the temperature of this stage is approximately consistent with that of the first rapid mass loss peak (Peak a) of the DTG curve in Fig. 1. At the same time, Fig. 5 just explains the predecomposition stage at 18.99 min as the release and decomposition of Fc in Fc- β -CD.

Finally, at 21.85 min (about 583 K) in Curve C, there is a sudden increase in the amount of fragments, strongly implying the effect of the presence of Fc on the thermal decomposition behavior of β -CD.

3.6. Thermal trace curves for the key fragment of m/z 60.02

The fragment of m/z 60.02 is one of the most important signals involving in the rupture of both C–C and C–O bonds in α -1,4-D-glucopyranosyl units of β -CD during the thermal decomposition process [26,31], and its MID curves in both free β -CD and Fc- β -CD are given in Fig. 7.

The peak shapes of the MID curves of the fragment of m/z 60.02 are considerably similar to those of the TIC curves of corresponding samples. It can be considered as the signal for the collapse of glucopyranose ring in free β -CD and Fc- β -CD. However, it is interesting to find that the initial temperature for the release process of the fragment in free β -CD (Curve A, about 553 K) is lower than that in Fc- β -CD (Curve B, about 568 K). This order is reverse to that of the decomposition of whole samples as previously described on the basis of results in TIC curves, which suggests again that the predecomposition stage in Fc- β -CD (Curve C, see Fig. 2) is caused by the

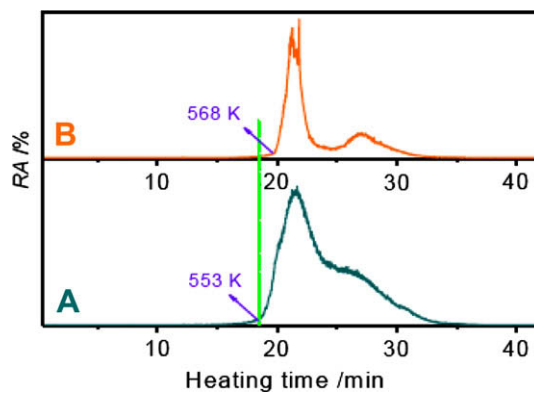


Fig. 7. MID curves of the fragment of m/z 60.02 from free β -CD (A) and Fc- β -CD (B).

release of Fc. Further, the delayed release of the fragment of m/z 60.02 indicates the positive influence of Fc on stabilizing the macrocyclic conformation of β -CD.

3.7. The decomposition process of the complexed β -CD in Fc- β -CD

First, when the sample is heated to 573 K and above, more small fragments with m/z values less than 200 are observed in Fig. 8.

According to Fig. 8A, the fragments of m/z 43.02 (RA, 9.10%), 60.02 (23.76%) and 73.03 (12.11%) are $\text{C}_2\text{H}_3\text{O}^+$, $\text{C}_2\text{H}_4\text{O}_2^+$ and $\text{C}_3\text{H}_5\text{O}_2^+$, respectively, which all come from β -CD [26,31]. And their RA values are gradually increased with the increasing temperature. For example, the RA value for the fragment of m/z 43.02 is increased from 9.10% at 20.54 min to 48.95% at 22.72 min while the strongest peak is the fragment signal of Fc^+ (m/z 186.01) all the time. It is known that the relative mass content of Fc is much lower than that of β -CD in its inclusion complex. Theoretically,

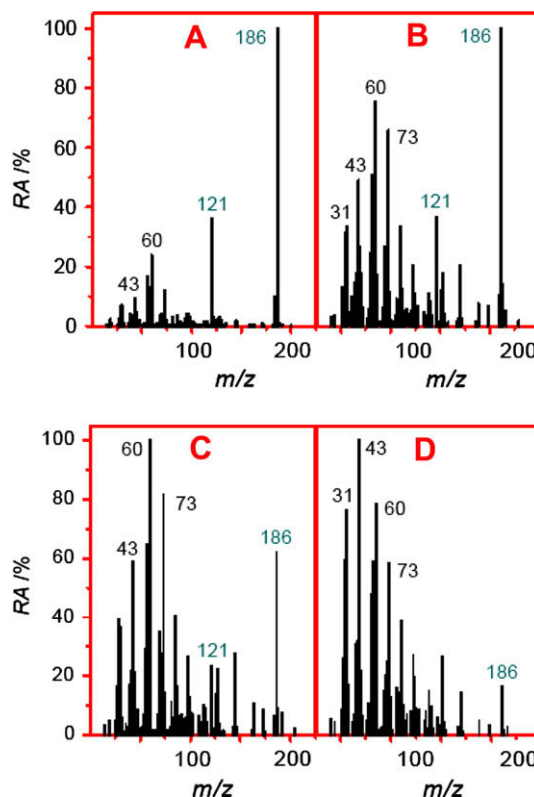


Fig. 8. Mass spectra of Fc- β -CD at 20.54 (A), 22.72 (B), 27.64 (C) and 31.42 min (D).

those fragment peaks resulting from the Fc should be very weak relative to those of β -CD if a great number of β -CD molecules are already decomposed into fragments.

Still the strongest peak in the spectrum of Fig. 8B is due to the fragment of m/z 186.01 at about 595 K, but the RA value of the typical fragment of m/z 60.02 has been increased to 75.26%. This phenomenon clearly reveals that before 22.42 min the decomposition of the sample is dominated by the complexed Fc, and this decomposition at around 22.42 min can be regarded as the beginning of the thermal decomposition stage for the complexed β -CD.

When the temperature is raised, clearly the decomposition of the complexed β -CD plays the leading role as seen in Fig. 8C and D. The RA values of the fragments from the complexed Fc are gradually decreased. For instance, the fragment of m/z 186.01 does not become the strongest one at 31.42 min. As a matter of fact, the increase of temperature also has a large influence on the decomposition behavior of the complexed β -CD in the light of the main fragment distribution in the figures. For example, the fragment signal of m/z 43.02 becomes the strongest peak at a higher temperature rather than the fragment of m/z 60.02. Besides, the first three strongest peaks in Fig. 8C: m/z 60.02 (RA, 100%), 73.03 (81.71%) and 57.03 (64.50%) are distinct from those in Fig. 8D: m/z 43.02 (RA, 100%), 60.02 (78.59%) and 31.02 (76.21%). This difference also occurred in our previous study [26], and is most likely due to the effect of temperature changes on the thermal decomposition modes of the complexed β -CD.

Two mass spectra of free β -CD at rapid decomposition stage are shown in Fig. 9. We find that the thermal decomposition process of

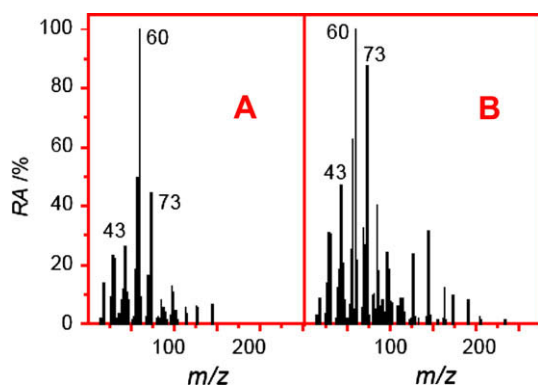


Fig. 9. Mass spectra of free β -CD at 19.60 (A) and 27.40 min (B).

free β -CD seems to occur in a major path. The mass spectra of free β -CD at different temperatures are all similar to each other during the heating process. For example, the fragments of m/z 60.02, 73.03 and 57.03 for free β -CD always indicate very strong signals in each case.

The decomposition mode of free β -CD is in approximately accordance with the initial decomposition stage of the complexed β -CD in Fc- β -CD. After compared the mass spectra of free β -CD at 19.60 with those of Fc- β -CD at 18.99 and 20.54 min, we find that the existence of Fc makes the decomposition process of the complexed β -CD quite slow in terms of the number and intensity of signals. According to the data of mass spectra, we think that the thermal decomposition mode of the complexed β -CD is completely different from what have existed in the past [26]. Two proposed possible decomposition modes of the complexed β -CD in Fc- β -CD are illustrated in Fig. 10.

The fragments of m/z 60.02 and 73.03 are the two key ones in mass spectra below 553 K. With the temperature enhancement, the formation of a smaller fragment $C_2H_3O^+$ (m/z 43.02) has the advantage on intensity variations from Fig. 8A–D. Interestingly, the fragment of CO_2^+ (m/z 43.99) appears only with a rather low RA value (<4.70%), which is greatly different from the previous observation [26]. Thus the destruction of the C–O bonds in α -1,4 linkages should be one of the major rupture forms during the heating process. From both the MID curve of the complexed Fc released from Fc- β -CD and the detailed data from the mass spectra of Fc- β -CD itself, we infer that the decomposition process of the complexed β -CD is accompanied with the release of Fc. This finding is significantly different from the prevailing opinion that an included guest by CD is released ahead of the decomposition of the CD molecules.

4. Conclusions

The present work provides an example depicting the relationship between heating temperatures and fragment compositions of a second-sphere coordination compound. It is found that the release of Fc is efficiently protected by the cavity of β -CD, and at the same time the decomposition modes of the complexed β -CD are greatly changed due to the interaction with Fc. Further, this study provides a paradigm that ferrocene decomposes in the β -CD cavity through the release of a $CpFe^+$ moiety, and the remaining Cp ring remains contained in the host. We believe that this work is important and significant to understand the nature of molecular aggregates of coordination compounds, as well as the decomposition

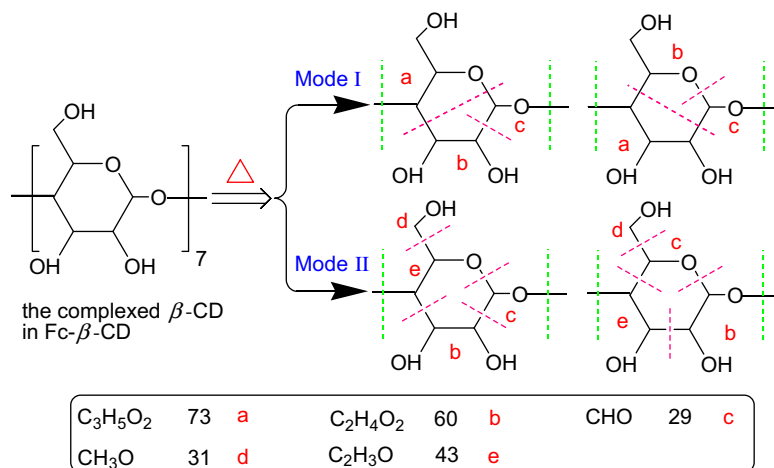


Fig. 10. Proposed decomposition modes of the complexed β -CD in Fc- β -CD.

and release behaviors of transition metal coordination compounds in molecular aggregates.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.10.014](https://doi.org/10.1016/j.jorganchem.2009.10.014).

References

- [1] A. Harada, M. Osaki, Y. Takashima, H. Yamaguchi, *Acc. Chem. Res.* 41 (2008) 1143–1152.
- [2] G. Wenz, B.H. Han, A. Muller, *Chem. Rev.* 106 (2006) 782–817.
- [3] L.X. Song, L. Bai, X.M. Xu, J. He, S.Z. Pan, *Coord. Chem. Rev.* 253 (2009) 1276–1284.
- [4] J. Marques, L. Anjo, M.P.M. Marques, T.M. Santos, F.A.A. Paz, S.S. Braga, *J. Organomet. Chem.* 693 (2008) 3021–3028.
- [5] M.V. Rekharsky, Y. Inoue, *Chem. Rev.* 98 (1998) 1875–1917.
- [6] R. Villalonga, R. Cao, A. Frago, *Chem. Rev.* 107 (2007) 3088–3116.
- [7] F.H. Huang, H.W. Gibson, *Prog. Polym. Sci.* 30 (2005) 982–1018.
- [8] D.P. Ferris, Y.L. Zhao, N.M. Khashab, H.A. Khatib, J.F. Stoddart, J.I. Zink, *J. Am. Chem. Soc.* 131 (2009) 1686–1688.
- [9] C. Machut-Binkowski, F. Hapiot, R. Cecchelli, P. Martin, E. Monflier, *J. Incl. Phenom. Macrocycl. Chem.* 57 (2007) 567–572.
- [10] S. Muratsugu, S. Kume, H. Nishihara, *J. Am. Chem. Soc.* 130 (2008) 7204–7205.
- [11] Y. Liu, R.Q. Zhong, H.Y. Zhang, H.B. Song, *Chem. Commun.* (2005) 2211–2213.
- [12] F. Hapiot, S. Tilloy, E. Monflier, *Chem. Rev.* 106 (2006) 767–781.
- [13] A. Harada, S. Takahashi, *J. Incl. Phenom.* 2 (1984) 791–798.
- [14] J.A. Fernandes, S. Lima, S.S. Braga, P. Ribeiro-Claro, J.E. Rodriguez-Borges, C. Teixeira, M. Pillinger, J.J.C. Teixeira-Dias, I.S. Goncalves, *J. Organomet. Chem.* 690 (2005) 4801–4808.
- [15] C.C.L. Pereira, C.V. Diogo, A. Burgeiro, P.J. Oliveira, M.P.M. Marques, S.S. Braga, F.A. Almeida Paz, M. Pillinger, S. Goncalves, *Organometallics* 27 (2008) 4948–4956.
- [16] Z. Petrovski, M.R.P.N. de Matos, S.S. Braga, C.C.L. Pereira, M.L. Matos, I.S. Goncalves, M. Pillinger, P.M. Alves, C.C. Romao, *J. Organomet. Chem.* 693 (2008) 675–684.
- [17] H.C. Canuto, A. Masic, N.H. Rees, S.J. Heyes, R. Gobetto, S. Aime, *Organometallics* 25 (2006) 2248–2252.
- [18] C.S. Lu, Z.P. Ni, W.L. Liu, Y. Zou, J.L. Xie, C.L. Ni, H.Z. Zhu, Q.J. Meng, Y.E. Yao, *J. Organomet. Chem.* 681 (2003) 269–274.
- [19] T.V. Mitkina, N.F. Zakharchuk, D.Y. Naumov, O.A. Gerasko, D. Fenske, V.P. Fedin, *Inorg. Chem.* 47 (2008) 6748–6755.
- [20] T.V. Mitkina, M.N. Sokolov, D.Y. Naumov, N.V. Kuratieva, O.A. Gerasko, V.P. Fedin, *Inorg. Chem.* 45 (2006) 6950–6955.
- [21] L.X. Song, H.M. Wang, X.Q. Guo, L. Bai, *J. Org. Chem.* 73 (2008) 8305–8316.
- [22] F. Giordano, C. Novak, J.R. Moyano, *Thermochim. Acta* 380 (2001) 123–151.
- [23] S.S. Braga, M.P.M. Marques, J.B. Sousa, M. Pillinger, J.J.C. Teixeira-Dias, I.S. Goncalves, *J. Organomet. Chem.* 690 (2005) 2905–2912.
- [24] L.X. Song, Z. Dang, *J. Phys. Chem. B* 113 (2009) 4998–5000.
- [25] L.X. Song, L. Bai, *J. Phys. Chem. B* 113 (2009) 9035–9040.
- [26] L.X. Song, P. Xu, *J. Phys. Chem. A* 112 (2008) 11341–11348.
- [27] V.T. Yilmaz, A. Karadağ, H. İçbudak, *Thermochim. Acta* 261 (1995) 107–118.
- [28] L.X. Song, C.F. Teng, P. Xu, H.M. Wang, Z.Q. Zhang, Q.Q. Liu, *J. Incl. Phenom. Macrocycl. Chem.* 60 (2008) 223–233.
- [29] H. Yoshii, T.L. Neoh, S.H. Beak, T. Furuta, *J. Incl. Phenom. Macrocycl. Chem.* 56 (2006) 113–116.
- [30] C. Yuan, Z.Y. Jin, X.M. Xu, H.N. Zhuang, W.Y. Shen, *Food Chem.* 109 (2008) 264–268.
- [31] P. Xu, L.X. Song, H.M. Wang, *Thermochim. Acta* 469 (2008) 36–42.