

A unique tetramer of 4 : 5 β -cyclodextrin–ferrocene in the solid state†

Yu Liu,* Rui-Qin Zhong, Heng-Yi Zhang and Hai-Bin Song

Received (in Cambridge, UK) 7th December 2004, Accepted 16th February 2005

First published as an Advance Article on the web 4th March 2005

DOI: 10.1039/b418220k

A single crystal of a unique 4 : 5 inclusion complex between β -cyclodextrin and ferrocene was prepared and the structure was determined by X-ray crystallographic analysis, showing that four of the five ferrocenes were included in the cavities of four β -cyclodextrins along the axial orientation of the tetramer, while another was co-included between two β -cyclodextrins from the equatorial orientation.

Cyclodextrins (CDs) can form stable inclusion complexes with a variety of guest molecules, in which the guest molecules are included within the hydrophobic cavities of the CDs.¹ One example of a class of nonpolar guest molecules that has been studied quite extensively with regard to CD hosts is the metallocene complexes,² especially ferrocene,³ for which there exist a variety of potential applications in optical, magnetic and superconducting materials and in catalysis due to their unusual properties. Although there are numerous reports describing the formation of stable inclusion complexes between CDs and ferrocene in solution and the solid state,^{3a,e,j,4} confirmatory structural information is still lacking.^{3r} On the other hand, it is well known that geometric rather than chemical factors are decisive in determining the kinds of guest molecules that can penetrate into the CD cavity. The internal diameter of β -CD is 7.0 Å, and the thickness of the ferrocene molecule is also thought to be *ca.* 7.0 Å.^{3j,r} Therefore, a 1 : 1 stoichiometry for ferrocene–(β -CD) complexes was always suggested. Here we report the first crystal structure analysis of the inclusion complex **1**,^{‡,§} of β -CD and ferrocene with a unique 4 : 5 inclusion ratio.

Complex **1** crystallizes in the monoclinic space group *C*2 and consists of four β -CD units (A, B, C and D), five ferrocenes and twenty-nine water molecules in a unit cell. As shown in Fig. 1, the four β -CDs form two dimeric motifs which are arranged down the same axial orientation to compose a tetramer. A very significant structural feature of the crystal is that the five ferrocenes interact with CDs in three distinct binding modes: (1) two of them are axially included into the hydrophobic cavity of CDs A and D respectively from the primary hydroxy side, (2) the other two ferrocenes are included from the secondary hydroxy side of B and C, and (3) the fifth ferrocene is equatorially co-included by the two dimers. Comparing with another tetramer reported by Nakanishi *et al.*,⁵ the distance between the O(4)-planes in each dimer is also 7.1 Å, but that between the dimers increases from 8.9 Å⁵ to 9.3 Å, which can be attributed to the insertion of the ferrocene molecule.

For those ferrocene molecules penetrating the cavities of the CDs, one of their cyclopentadienyl rings falls in the O(4)-plane of

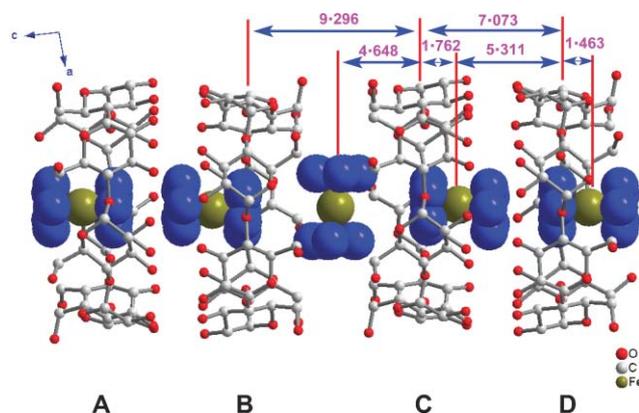


Fig. 1 Column structure of **1** composed of four symmetry-related β -CDs (A, B, C, and D) and five ferrocenes, viewed from the diagonal of the *ac* plane (water molecules are omitted for clarity). The distances (Å) between the O(4) atom planes of CDs and the iron atoms in the ferrocenes are shown. The color of the carbon atoms in the ferrocenes is shown in blue, distinguishing them from those in the CDs.

the CD with a slight shift of *ca.* 0.15 Å. Although the original skeleton of every CD moiety with an approximate 7-fold axis and a round shape is not significantly changed on complexation of ferrocene, all of the ferrocene molecules do deform to some extent. The distance between the two cyclopentadienyl rings in the ferrocene co-included by the two dimers is elongated from 3.41 Å⁶ to 3.52 Å, whereas those in CDs A and D as well as B and C are compressed to 3.25 Å and 3.19 Å, respectively. It should be noted that the five iron atoms in these ferrocenes are all located along the axis of the tetramer, and the adjacent ferrocenes included in the dimers are stacked through strong face-to-face π – π aromatic stacking interactions with distances of *ca.* 3.48 Å, while the middle ferrocene molecule which is co-included by the two dimers interacts with its adjacent ferrocene molecules in an edge-to-face orientation ($d = 2.668$ Å for the C–H $\cdots\pi$ interaction).⁷ The arene groups are generally slightly offset to each other, so the present observation is interesting. This may be because a head-to-head arrangement of the two CDs might have forced these ferrocenes to take such a structure.

The crystal structures of CD inclusion complexes reported hitherto have been broadly classified into three packing arrangements.^{1c} One is the cage-type in which guest molecules are small and fully enclosed in the CD cavity, and the complex molecules stack in a “herringbone” fashion. Another is the channel-type in which CD units stack in infinite columns by either “head-to-head” or “head-to-tail” contacts between units, and the CD cavities are aligned to produce continuous channels. The third observed structure is the layer-type in which the macrocyclic ring planes of

† Electronic supplementary information (ESI) available: crystal data and structure refinement, packing structures and XRPD pattern for **1**. See <http://www.rsc.org/suppdata/cc/b4/b418220k/>
*yuliu@public.tpt.tj.cn

CDs are in parallel orientation, with alternate layers shifted laterally to produce a pattern described as “bricks in a wall”. In the crystal structure of **1**, we have identified a tetrameric arrangement consisting of two head-to-head dimeric structures. Individual tetrameric units act as the steps of staircase trajectories along the crystallographic *c* axis with a distance of *ca.* 3.43 Å between steps, leading to the formation of a channel-type quasi-column (Fig. 2 and 3). The distance between two neighboring CDs from adjacent tetrameric units is 9.1 Å, which is longer than the distance within each dimer and shorter than the distance between the dimers within the tetrameric unit; no hydrogen bond among the primary hydroxyl groups of CDs is found. A closer analysis reveals that the quasi-column is held together by offset face-to-face π - π stacking interactions between ferrocenes in adjacent tetramers with a distance of *ca.* 2.95 Å. That is to say, the offset stacking interactions play an important role to form the channel-type quasi-column.

β -CD has a strong tendency to form head-to-head dimeric units.⁸ The solid state packing arrangements made by these dimeric complex units are classified as four distinct classes of packing mode, *i.e.*, channel type (CH), intermediate type (IM), chessboard type (CB), and screw-channel type (SC).⁹ What is interesting is that the two dimeric units in the tetramer pack in CH mode, and then the tetrameric units pack in IM mode. Referring to M. R. Caira’s work,¹⁰ the X-ray powder pattern of complex **1** is different from those of crystals in CH mode or *C2* space group, but is similar to those of crystals in IM mode or *P1* space group only when $2\theta > 10^\circ$, indicating that the discontinuous channels formed by close-packed layers of tetramers stacking with an obvious lateral shift is the main characteristic of complex **1**.

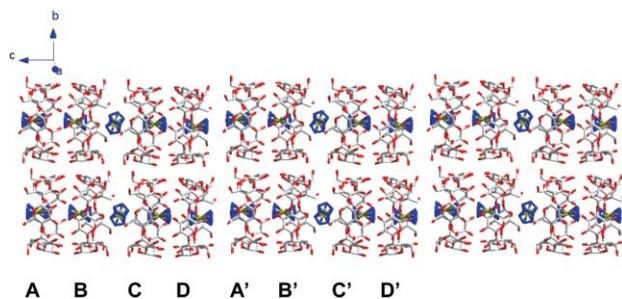


Fig. 2 Channel-type molecular packing of **1** (water molecules are omitted for clarity).

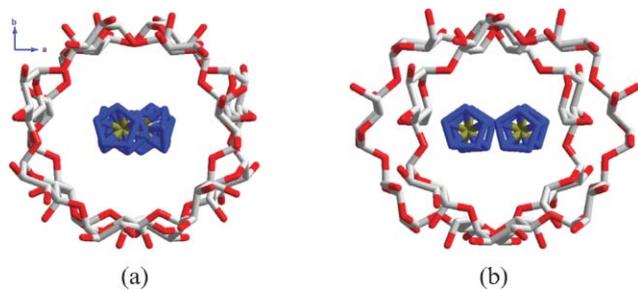


Fig. 3 The stacking structures of **1** viewed down the *c* axis: (a) CDs B and C, and (b) CDs D and A'. Ferrocenes included in these CDs as well as that co-included by the two dimers are also shown.

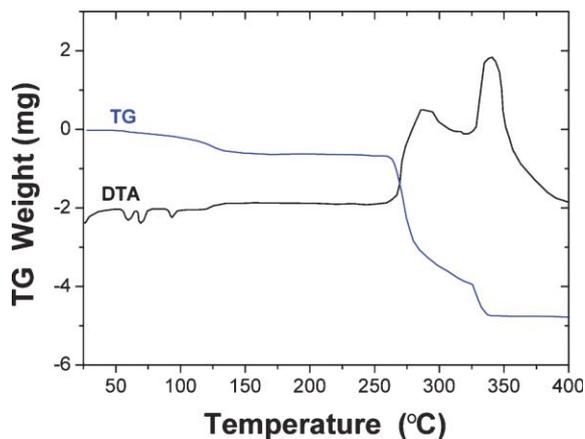


Fig. 4 The thermogravimetric (TG) and differential thermal analysis (DTA) for **1**.

The thermal behavior of complex **1** was studied from room temperature to 400 °C (Fig. 4). The thermogravimetric (TG) data showed that the complex dehydrates at about 59 °C, and then releases one ferrocene at about 94 °C. Free ferrocene sublimates at 88 °C,¹¹ so one might deduce reasonably that the lost ferrocene should be the ferrocene molecule co-included by two dimers. At *ca.* 262 °C, the rest dissociates. This temperature is lower than not only the mp of the β -CD component, but also the decomposition temperature of the 1 : 1 stoichiometric inclusion compound of β -CD and ferrocene,^{3c,h} which could be attributed to the ferrocene molecules not being included completely in the cavities of the β -CDs.

In summary, we have prepared a 4 : 5 stoichiometry inclusion complex between β -CD and ferrocene by hydrothermal treatment, which is distinctly different from those observed in the solution or solid phase. Thus the complex’s stoichiometry is not a simple function of the size-fit concept but is influenced substantially by the temperature of treatment systems. These observations open the door for controlling the formation of supramolecular complexes by changing reaction conditions.

This work was supported by the National Natural Science Foundation (Nos. 90306009, 20272028), and the Tianjin Natural Science Foundation (No. 043604411).

Yu Liu,* Rui-Qin Zhong, Heng-Yi Zhang and Hai-Bin Song

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China.
E-mail: yuliu@public.tpt.tj.cn

Notes and references

‡ The inclusion complex was prepared by dissolving β -CD and ferrocene in a 1 : 2 molar ratio in a minimum amount of water in a Teflon-lined stainless bomb, which was sealed and then heated at 100 °C under hydrothermal conditions for 2 days. When the solution was cooled to room temperature after 10 h, orange-yellow crystals suitable for X-ray data collection were obtained.

§ X-ray single-crystal diffraction data for complex **1** were collected on a Bruker Smart 1000 CCD diffractometer at 293(2) K with Mo-K α radiation ($\lambda = 0.71073$ Å) by φ - ω scan mode. The program SAINT (*SAINT Software Reference Manual*, Bruker AXS, Madison, WI, 1998.) was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied using SADABS program).

(Sheldrick, G. M. *SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.) Metal atoms in each complex were located from the *E*-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2 . All hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The Fe atom of the ferrocene between β -CD dimers is located on a two-fold axis and carbon atoms are disordered, with occupancies of 0.5 and 0.5 in two sites. *Crystal data for 1*: $C_{109}H_{194}Fe_{2.5}O_{84.50}$ $M = 2996.27$, monoclinic, space group $C2$, $a = 19.378(5)$, $b = 24.094(6)$, $c = 32.776(9)$ Å, $\beta = 93.963(5)^\circ$, $V = 15266(7)$ Å³, $Z = 4$ $D_c = 1.304$ g cm⁻³, 38848 reflections measured, 25259 unique ($R_{int} = 0.0503$), final $R1 = 0.1021$, $wR2 = 0.2424$ for 10763 independent reflections [$I > 2\sigma(I)$]. CCDC 244423. See <http://www.rsc.org/suppdata/cc/b4/b418220k/> for crystallographic data in .cif or other electronic format.

- 1 (a) M. L. Bender and M. Komiyama, *Cyclodextrin Chemistry*, Springer-Verlag, New York, 1978; (b) G. Wenz, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 803; (c) K. Harata, *Chem. Rev.*, 1998, **98**, 1803; (d) S. A. Nepogodiev and J. F. Stoddart, *Chem. Rev.*, 1998, **98**, 1959; (e) F. M. Raymo and J. F. Stoddart, *Chem. Rev.*, 1999, **99**, 1643; (f) A. Harada, *Acc. Chem. Res.*, 2001, **34**, 456.
- 2 (a) D. R. Alston, A. M. Z. Slawin, J. F. Stoddart and D. J. William, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 786; (b) H. M. Colquhoun, J. F. Stoddart and D. J. William, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 487.
- 3 (a) A. Harada and S. Takahashi, *J. Inclusion Phenom.*, 1984, **2**, 791; (b) Y. Maeda and Y. Takashima, *J. Inclusion Phenom.*, 1984, **2**, 799; (c) A. Harada and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1984, 645; (d) A. Ueno, F. Moriwaki, T. Osa, F. Hamada and K. Murai, *Tetrahedron Lett.*, 1985, **26**, 899; (e) T. Matsue, D. H. Evans, T. Osa and N. Kobayashi, *J. Am. Chem. Soc.*, 1985, **107**, 3411; (f) N. Kobayashi and T. Osa, *Chem. Lett.*, 1986, 421; (g) T. Matsue, T. Kato, U. Akiba and T. Osa, *Chem. Lett.*, 1986, 843; (h) A. Harada, Y. Hu, S. Yamamoto and S. Takahashi, *J. Chem. Soc., Dalton Trans.*, 1988, 729; (i) V. V. Strelets, I. A. Mamedjarova, M. N. Nefedova, N. I. Pysnograeva, V. I. Sokolov, L. Pospisil and J. Hanzlik, *J. Electroanal. Chem.*, 1991, **310**, 179; (j) R. Isnin, C. Salam and A. E. Kaifer, *J. Org. Chem.*, 1991, **56**, 35; (k) S. McCormack, N. R. Russell and J. F. Cassidy, *Electrochim. Acta*, 1992, **37**, 1939; (l) A. E. Kaifer, in *Transition Metals in Supramolecular Chemistry*, ed. L. Fabrizzi and A. Poggi, NATO ASI Series, Kluwer, Dordrecht, The Netherlands, 1994, pp. 227–243; (m) V. T. Yilmaz, A. Karadağ and H. İbBudak, *Thermochim. Acta*, 1995, **261**, 107; (n) J. H. T. Luong, R. S. Brown and P. M. Schmidt, *J. Mol. Recognit.*, 1995, **8**, 132; (o) L. A. Godinez, P. Sonal, C. M. Criss and A. E. Kaifer, *J. Phys. Chem.*, 1995, **99**, 17449; (p) R. M. Nielson, L. A. Lyon and J. T. Hupp, *Inorg. Chem.*, 1996, **35**, 970; (q) R. Castro, I. Cuadrado, B. Alonso, C. M. Casado, M. Moran and A. E. Kaifer, *J. Am. Chem. Soc.*, 1997, **119**, 5760; (r) Y. Odaki, K. Hirotsu, T. Higuchi, A. Harada and S. Takahashi, *J. Chem. Soc. Perkin Trans. 1*, 1990, 1230; (s) R. C. Sabapathy, S. Bhattacharyya, W. E. Clenland, Jr and C. L. Hussey, *Langmuir*, 1998, **14**, 3797.
- 4 (a) F. M. Menger and M. J. Sherrod, *J. Am. Chem. Soc.*, 1988, **110**, 8606; (b) H. J. Thiem, M. Brandl and R. Breslow, *J. Am. Chem. Soc.*, 1988, **110**, 8612; (c) R. Breslow, M. F. Czarniecki, J. Emert and H. Hamaguchi, *J. Am. Chem. Soc.*, 1980, **102**, 762; (d) B. Sigel and R. Breslow, *J. Am. Chem. Soc.*, 1975, **97**, 6869; (e) L. A. Godínez, S. Patel, C. M. Criss and A. E. Kaifer, *J. Phys. Chem.*, 1995, **99**, 17449; (f) E. Coutouli-Argyropoulou, A. Kelaidopoulou, C. Sideris and G. Kokkinidis, *J. Electroanal. Chem.*, 1999, **477**, 130; (g) D. Osella, A. Carretta, C. Nervi, M. Ravera and R. Gobetto, *Organometallics*, 2000, **19**, 2791.
- 5 I. Nakanishi, M. Arai, T. Fujiwara and K.-I. Tomita, *J. Inclusion Phenom.*, 1984, **2**, 689.
- 6 D. Braga and F. Grepioni, *Organometallics*, 1992, **11**, 711.
- 7 (a) I. Dance, in *Encyclopedia of Supramolecular Chemistry*, ed. J. L. Atwood and J. W. Steed, Marcel Dekker, New York, 2004, pp. 1067–1092; (b) S. L. James, in *Encyclopedia of Supramolecular Chemistry*, ed. J. L. Atwood and J. W. Steed, Marcel Dekker, New York, 2004, pp. 1093–1099; (c) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5527; (d) G. R. Desiraju and A. Gavezzotti, *J. Chem. Soc., Chem. Commun.*, 1989, 621; (e) A. Gavezzotti, *Chem. Phys. Lett.*, 1989, **161**, 67; (f) I. Dance and M. Scudder, *New J. Chem.*, 1998, **22**, 481; (g) C. A. Hunter, *Chem. Soc. Rev.*, 1994, 101; (h) M. Nishio, *CrystEngComm.*, 2004, **6**, 130.
- 8 W. Saenger, *J. Inclusion Phenom.*, 1984, **2**, 445.
- 9 D. Mentzafos, I. M. Mavridis, G. Le Bas and G. Tsoucaris, *Acta Crystallogr., Sect. B*, 1991, **47**, 746.
- 10 M. R. Caira, *Rev. Roum. Chim.*, 2001, **46**, 371.
- 11 V. T. Yilmaz, A. Karadağ and H. İbBudak, *Thermochimica Acta*, 1995, **261**, 107.