Preparation and Properties of Cyclodextrin–Ferrocene Inclusion Complexes

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One-to-one inclusion complexes were obtained in a crystalline state in high yield by the treatment of β- and γ-cyclodextrin (CD) with ferrocene (FcH) and its derivatives (FcR), while α-cyclodextrin formed 2 : 1 [CD : FcR (FcH)] complexes with ferrocene and the monosubstituted derivatives.

Cyclodextrins (α-, β-, and γ-CD) form inclusion complexes with various compounds, ranging from organic molecules to small ions, and even rare gases.[1] However, there are only a few reports on the interaction between organometallic compounds and cyclodextrins. Breslow *et al.* reported high acylation rates for β-CD using ferrocene derivatives and assumed β-CD–substrate complexes as intermediates.[2] We report here the preparation and characterization of cyclodextrin–ferrocene inclusion complexes as an example of CD inclusion complexes of organotransition metal compounds.

Since ferrocene, FcH, and its derivatives, FcR, are insoluble in water, a co-crystallization method from aqueous solution, which is usually employed with water-soluble substrates, cannot be used in this case. Several methods were tried to obtain CD–ferrocene inclusion complexes, and we found that direct addition of fine ferrocene crystals to a CD aqueous solution at 60 °C with stirring gives inclusion complexes in high yields. Using this method we obtained inclusion complexes of α-, β-, and γ-CD with substituted ferrocenes

such as acetylferrocene, FcAc, 1,1'-diacetylferrocene Fc(Ac)₂, and α-hydroxyethylferrocene. However, although α-CD did not form complexes with the 1,1'-disubstituted derivative, it did form complexes with ferrocene and the monosubstituted derivatives. The CD–ferrocene complexes were characterized by elemental analyses, and i.r., u.v., and ¹H n.m.r. spectra. Stoicheiometries were determined by elemental analyses, including atomic absorption analysis of the Fe contents, which show that all the complexes obtained here are stoicheiometric compounds and have definite ratios of CD : FcR depending on the combination of host and guest. β-CD formed 1 : 1 complexes with ferrocene and its derivatives regardless of the molar ratio of the host to guest in the reaction, indicating that the interaction between cyclodextrin and ferrocene is a real inclusion phenomenon (Table 1). γ-CD also formed 1 : 1 complexes, while α-CD gave 2 : 1 [α-CD : FcH (FcR)] complexes in high yields even if α-CD was treated with excess of FcH or FcR. A consideration of the molecular dimensions of α-CD and ferrocene implies that the

Table 1. Preparation of CD–ferrocene inclusion complexes.

CD	FcR	Molar ratio of CD : FcR	Product Yield/%	Product CD : FcR
α	FcH	2 : 1	68	2 : 1
α		1 : 1	75	2 : 1
α		1 : 4	70	2 : 1
β		2 : 1	85	1 : 1
β		1 : 1	56	1 : 1
β		1 : 4	100	1 : 1
γ		1 : 1	59	1 : 1
γ		1 : 5	67	1 : 1
α	FcAc	1 : 2	73	2 : 1
β		1 : 2	100	1 : 1
γ		1 : 2	74	1 : 1
α	Fc(Ac)₂	1 : 2	0	—
β		1 : 2	74	1 : 1
γ		1 : 2	90	1 : 1

Figure 1. (a) α-CD–FcH, 2 : 1 complex; (b) β-CD–FcH, 1 : 1 complex; (c) γ-CD–FcH, 1 : 1 complex.

ferrocene molecule is too large to be completely included in a single α-CD cavity, which can accommodate only one cyclopentadienyl ring. A ferrocene molecule appears to fit well into the cavity formed by two molecules of α-CD.

β-CD–FcH and γ-CD–FcH complexes are so stable that they can be recrystallized from water to give yellow crystals. α-CD–FcH and β-CD–FcH complexes are thermally stable and do not liberate ferrocene on heating at 100 °C *in vacuo*. Thermogravimetric analyses showed that these complexes are stable up to 200 °C and decompose around the m.p. of the CD component. Absorption and c.d. spectra of the complexes were measured in solution. A large positive induced Cotton effect was observed in the case of the β-CD–FcH complex, while the γ-CD–FcH complex showed a negative spectrum. These results indicate that the orientation of the ferrocene molecule in the cavity of β-CD is different from that in the γ-CD complex.[3] Molecular models of the CDs and ferrocene
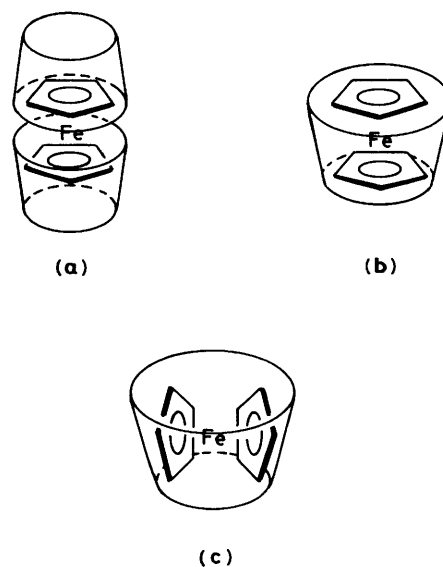
indicate that a ferrocene molecule could fit well into a β-CD cavity by axial inclusion, while a γ-CD cavity is large enough to accommodate a ferrocene molecule equatorially. Proposed structures for the complexes are shown in Figure 1.

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