

Disposition of Ferrocenes in β - or γ -Cyclodextrin

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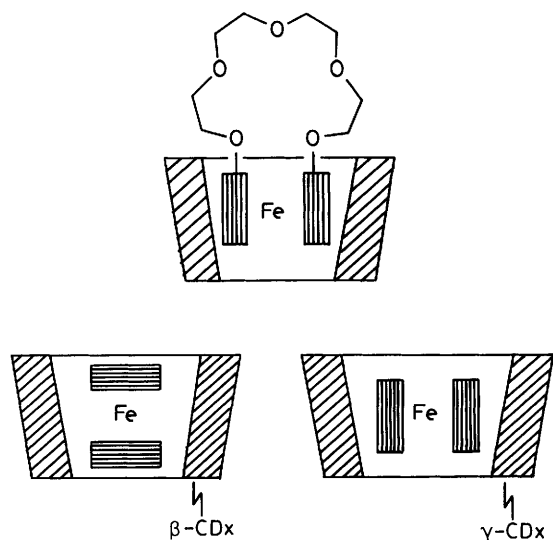
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The inclusion of ferrocene in β - or γ -cyclodextrin (β -CDx or γ -CDx) has been determined to be axial or equatorial, respectively, by comparing the induced circular dichroism (i.c.d.) of 1,4,7,10,13-pentaoxa[13]ferrocenophane (**1**) in the presence of β -CDx with that of ferrocene in β -CDx or γ -CDx.

Induced circular dichroism (i.c.d.) has been successfully applied to the structural elucidation of cyclodextrin (CDx)-chromophore host-guest complexes. In particular, the disposition of guest molecules in CDx-chromophore 1:1 complexes has been inferred based on the knowledge that electronic transitions parallel to the molecular axis of CDxs produce positive i.c.d. while those normal to the axis show negative i.c.d.¹ In the case of ferrocene (Fc)-CDx 1:1 complexes, however, the disposition of Fcs has not been determined, in spite of much work.² As indicated recently by calculations,^{2h} Fc can bind, for example, to β -CDx in both an axial and equatorial orientation, since the energy difference is too small to be significant. In fact it has been previously shown experimentally^{2g} that the disposition of ferrocenemono-carboxylic acid in β -CDx could be altered by a change in pH of the solution. If the polarization directions of the bands of Fcs were known, their orientation in CDxs might be determined from the sign of i.c.d. spectra; however, there has been uncertainty in both these parameters. In this study, we have prepared compound (**1**)³ and measured its i.c.d. spectrum in the presence of β -CDx. For this molecule, only equatorial inclusion is possible owing to size limitations, so that the disposition of Fcs in various CDxs can be conjectured by comparing their i.c.d. spectra with the i.c.d. spectrum of (**1**) in the presence of β -CDx.

Figure 1 shows the UV-VIS absorption and i.c.d. spectra of (**1**) in the presence of β -CDx in ethylene glycol. The shape of the absorption spectrum is similar to that of Fc (Figure 2), indicating that the attached crown unit does not affect the electronic structure of the Fc chromophore significantly. A negative and a positive i.c.d. peak correspond to absorption peaks at ~ 430 and ~ 220 nm, respectively. The band in the longest wavelength region (*ca.* 380–550 nm) has been proposed to contain two components with absorption maxima at around 420–430 nm and 460–470 nm, and both are assigned as d-d transitions.⁴ The intense peak at around 200–220 nm has been assigned to either a relatively pure π - π^* transition in the cyclopentadienyl (Cp) rings^{4a} or a charge-transfer band between the Cp rings and iron(II).^{4b,c} The interpretation of other regions of the spectra is also not consistent among different researchers. Although the polarization directions of these bands have not been clarified, the results shown in Figure 1 indicate that a negative i.c.d. appears between *ca.* 380 and 550 nm on equatorial inclusion of an Fc molecule.

Figure 2 shows the spectra of Fc- β -CDx and Fc- γ -CDx 1:1 complexes^{2c} in ethylene glycol. The absorption spectra have peaks at around 200, 250–260, and 400 nm and shoulders at ~ 300 nm. The i.c.d. spectra of these complexes are interesting in that their signals are opposite over a wide range of wavelengths. Except at 300–370 nm, Fc- β -CDx produces



Compound (1) and ferrocene included in cyclodextrins. The shaded rectangles represent C_5H_5 rings.

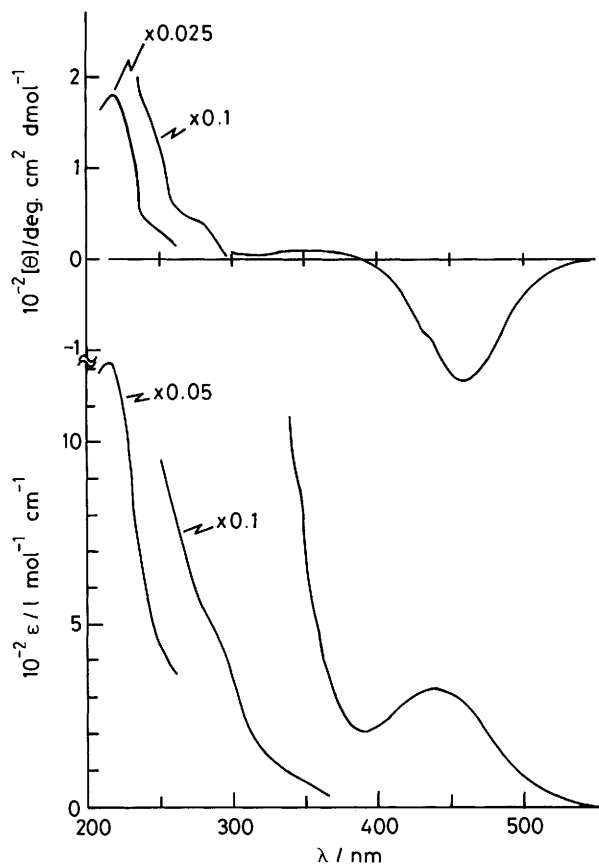


Figure 1. I.c.d. (top) and UV-VIS (bottom) spectra of (1) in the presence of β -CDx in ethylene glycol. $[(1)] = 9.98 \times 10^{-4}$ and $[\beta\text{-CDx}] = 0.020$ M.

positive i.c.d. peaks or shoulders associated with each absorption peak and shoulder, whilst Fc- γ -CDx shows negative i.c.d. over a wide range of wavelengths. By comparing the i.c.d. signal at *ca.* 380–550 nm with that of (1) in Figure 1, the inclusion of Fc is conjectured to be almost axial in Fc- β -CDx,

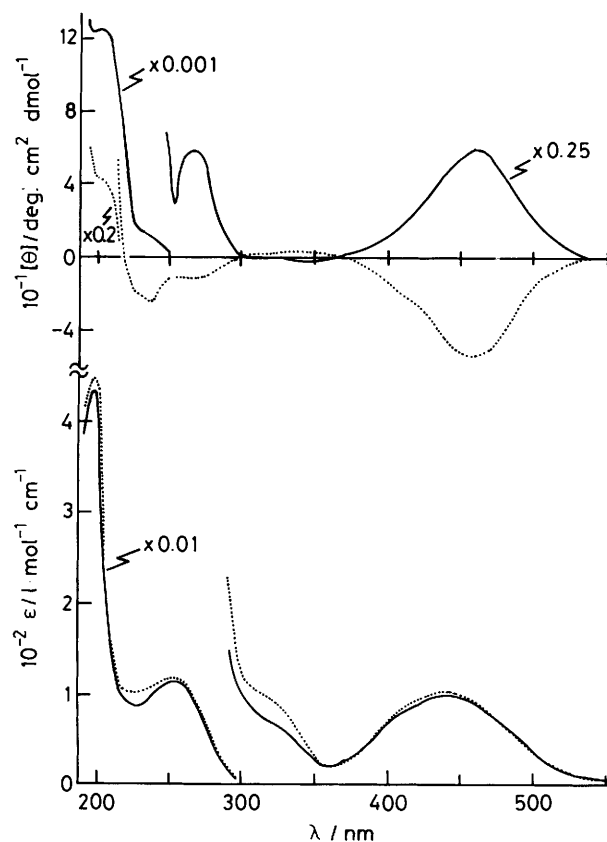


Figure 2. I.c.d. (top) and UV-VIS (bottom) spectra of Fc- β -CDx (—) and Fc- γ -CDx (.....) 1:1 complexes in ethylene glycol. $[\text{Fc-}\beta\text{-CDx}] = [\text{Fc-}\gamma\text{-CDx}] = 0.01$ M.

while equatorial in Fc- γ -CDx.[†] Thus it will be possible to judge the disposition of Fc derivatives in CDxs from the sign of the i.c.d. signal at *ca.* 380–550 nm (plus, axial; minus, equatorial).

In order to exemplify the importance of i.c.d. spectra in determining the orientation of guest molecules in CDxs, those for which the polarization directions of the absorption bands were predetermined have been employed to date;¹ the present study further shows that i.c.d. can be applicable even to compounds for which these have not been predetermined. By modifying the structure of a guest molecule to one which is suitable for only one inclusion mode and by measuring the i.c.d. spectrum of the resultant host-guest 1:1 complex, we have first obtained the relationship between the orientation of the guest molecule and the sign of the i.c.d. signal. Using this relationship as a model, the orientation of similar guest molecules in various CDxs can be evaluated by comparing their i.c.d. spectra. Also, it becomes possible to obtain information on the polarization of the absorption bands of the guest molecule. For example, the band of Fc at *ca.* 380–550 nm may be polarized roughly along the long axis of Fc molecule, since the i.c.d. signal in this region is negative when

[†] In order to support this conclusion, 500 MHz ^1H NMR spectra were recorded in deuterated dimethyl sulphoxide (DMSO), *N,N*-dimethylformamide (DMF), and their mixtures with water ($^2\text{H}_2\text{O}$). However, complexation did not occur in pure DMF, and in DMSO or DMSO- $^2\text{H}_2\text{O}$ mixtures the signals were hidden by large signals due to H_2O in DMSO.

the long axis of Fc is approximately normal to the axis of β -CDx (Figure 1).

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