Molecular Encapsulation of Half-Sandwich Complexes of Iron with Cyclodextrins: New Laminar Materials

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Abstract. The treatment of β- and γ-cyclodextrins with the half-sandwich complexes of iron afford the inclusion compounds $CpFe(L_2)X \cdot CD$ (β and γ) (X = Cl, I; L = CO; L_2 = dppe, dppe = $(Ph)_2P(CH_2)_2P(Ph)_2$), $[CpFe(L_2)L'] PF_6 \cdot CD$ (β and γ) L' neutral donor ligands and $[(Cp(dppe)Fe)_2 - \mu - CN]PF_6 \cdot 2CD$ (β and γ). The inclusion compounds $[Cp(dppe)Fe-NCCH_3]PF_6 \cdot \gamma$-CD and $[Cp(dppe)Fe-(\eta^1-dppm)]PF_6 \cdot \gamma$-CD have a laminar structure. The β- and γ-cyclodextrin encapsulation effect on the electro-oxidation of the binuclear complex was studied using cyclic voltammetry. The electron-transfer reactions associated with the oxidation of the two different N-bonded and C-bonded organometallic fragments are substantially affected by β and γ encapsulation.

Key words: Cyclodextrin inclusion compounds, organometallic, laminar compounds.

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six, seven or eight (1 → 4)-linked α-D-glucopyranose residues (α-, β-, γ-CD respectively) [1,2]. They are known to form inclusion compounds with a wide variety of guest molecules including transition-metal complexes [3–11]. As a consequence of the relatively nonpolar character of the CD cavity, transition metal complexes bearing hydrophobic ligands should be particularly suitable guests.

One of the most widely used hydrophobic ligands in transition metal chemistry is the cyclopentadienyl (η^5-C_5H_5) ligand [12]. This ring can penetrate the CD cavity, as shown by several recent reports [3,5,8–11]. Since the first report on adduct formation between ferrocene and β-cyclodextrin in 1975 [10], numerous papers have appeared in the literature describing α-, β-, and γ-cyclodextrin inclusion complexes with metallocenes as guest [8–11]. However, relatively few examples of cyclodextrin inclusion compounds with half-sandwich complexes have been reported [3,11]. Some of these compounds exhibit interesting nolinear optical properties [13]. In our laboratories a series of cyclopentadienyl [bis(diphenylphosphino)ethane]iron(II) complexes have recently been investigated [14–17]. Our interest in binuclear com-

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pounds containing this type of fragment, in relation to electron transfer [18a,b] in the solid state, has led us to investigate their potential as guest molecules for cyclodextrins. A part of this work has appeared in a preliminary communication [19].

2. Experimental

2.1. GENERAL

The mononuclear Cp(CO)$_2$FeCl [12], Cp(dppe)FeI [17], [Cp(dppe)Fe-NCCH$_3$]PF$_6$ [17], [Cp(dppe)Fe-(η^1-dppm)]PF$_6$ [16] and the binuclear [Cp(dppe)Fe-NC-Fe(dppe)Cp]PF$_6$ [18a] compounds were prepared by methods previously reported. β- and γ-cyclodextrin (Aldrich) were used as received. The solvents used were purified by standard procedures.

2.2. APPARATUS AND MEASUREMENTS

NMR spectra were measured with a Bruker AMX 300 instrument using DMSO as solvent. Chemical shifts are given relative to TMS (^{1}H) or 85% H$_3$PO$_4$ (^{31}P proton decoupled) with the shift reference being positive. IR spectra were recorded on a FT-IR Perkin-Elmer 2000 spectrophotometer in KBr discs. UV-visible spectra were recorded on a DMS-90 spectrophotometer in cuvettes of 1 cm length. Powder X-ray diffractograms were recorded in the range $2° > 2\theta > 50°$ on a Siemens D-5000 diffractometer using CuK_α radiation (40 kV, 30 mH) and a graphite mono-chromator ($\lambda = 1.5418$ Å). Samples were ground to a fine powder in order to reduce the likelihood of the crystallites exhibiting a preferred orientation. Scanning Electron Microphotographs were obtained on a Philips EM 300 instrument, using an aluminium support for the sample and a gold cover.

Electrochemical measurements were carried out on a Parc model 370 electrochemistry system, using a three electrode device, employing a glassy carbon working electrode, wire, counter electrode and saturated calomel reference electrode. Solutions were 10^{-3} M in the complex and 0.1 M [NBu$_4$]PF$_6$ was used as supporting electrolyte. Under the same experimental conditions, $E_{1/2}$ for the ferrocene/ferrocenium complex was 0.64 V with a peak separation of about 0.060 V (internal standard).

2.3. PREPARATION OF THE INCLUSION COMPOUNDS: GENERAL PROCEDURE

Compound 5. A solution containing 0.08 g (0.12 mmol) of Cp(dppe)FeI in ca. 5 mL of CH$_2$Cl$_2$ was layered on a stirred saturated aqueous solution of the cyclodextrin, 0.3 g (0.23 mmol) at 40 °C. After 15 min the cream solid formed at the interface, together with the solution, was centrifuged and the supernatant extracted with a syringe. The solid was then washed several times with CH$_2$Cl$_2$ and then with water. The solid residue was dried in vacuo.

The procedure for the preparation of the other compounds is similar to the above method. Data for the other compounds are as follows:

Compound 1. $Cp(CO)_2FeCl$ 0.04 g, 0.19 mmol, β-CD 0.4 g, 0.35 mmol. Yield 0.21 g, 75%. *Anal. Calc.* for $C_7H_5O_2ClFe\cdot(C_{42}H_{70}O_{35})\cdot8H_2O$. 39.43%C, 6.10%H. *Found* 39.32%C, 6.19%H.

Compound 2. $Cp(CO)_2FeI$ 0.07 g, 0.23 mmol, β-CD 0.5 g, 0.44 mmol. Yield 0.17 g, 49%. *Anal. Calc.* for $C_7H_5O_2IFe\cdot(C_{42}H_{70}O_{35})\cdot5H_2O$. 38.46%C, 5.56%H. *Found* 38.71%C, 5.91%H.

Compound 3. $Cp(CO)_2FeI$ 0.06 g, 0.20 mmol, γ-CD 0.5 g, 0.39 mmol. Yield 0.19 g, 54%. *Anal. Calc.* for $C_7H_5O_2IFe\cdot(C_{48}H_{80}O_{40})\cdot9H_2O$. 37.44%C, 5.84%H. *Found* 37.45%C, 6.09%H.

Compound 4. $Cp(dppe)FeI$ 0.14 g, 0.22 mmol, β-CD 0.5 g, 0.44 mmol. Yield 0.27 g, 58%. *Anal. Calc.* for $C_{31}H_{29}P_2IFe\cdot(C_{42}H_{70}O_{35})\cdot22H_2O$. 40.24%C, 6.57%H. *Found* 40.28%C, 6.50%H.

Compound 5. $Cp(dppe)FeI$ 0.08 g, 0.12 mmol, γ-CD 0.3 g, 0.23 mmol. Yield 0.16 g, 56%. *Anal. Calc.* for $C_{31}H_{29}P_2IFe\cdot(C_{48}H_{80}O_{40})\cdot21H_2O$. 40.84%C, 6.51%H. *Found* 40.76%C, 6.53%H.

Compound 6. $[Cp(dppe)Fe-NCCH_3]PF_6$ 0.06 g, 0.08 mmol, β-CD 0.2 g, 0.18 mmol. Yield 0.12 g, 63%. *Anal. Calc.* for $C_{33}H_{32}F_6P_3NFe\cdot(C_{42}H_{70}O_{35})\cdot21H_2O$. 40.56%C, 6.49%H. *Found* 40.93%C, 6.21%H.

Compound 7. $[Cp(dppe)Fe-NCCH_3]PF_6$ 0.05 g, 0.08 mmol, γ-CD 0.15 g, 0.11 mmol. Yield 0.10 g, 60%. *Anal. Calc.* for $C_{33}H_{32}F_6P_3NFe\cdot(C_{48}H_{80}O_{40})\cdot19H_2O$. 41.45%C, 6.40%H. *Found* 41.41%C, 7.78%H.

Compound 8. $[Cp(dppe)Fe-(\eta^1-dppm)]PF_6$ 0.14 g, 0.13 mmol, β-CD 0.3 g, 0.26 mmol. Yield 0.22 g, 58%. *Anal. Calc.* for $C_{56}H_{51}F_6P_5Fe\cdot(C_{42}H_{70}O_{35})\cdot35H_2O$. 41.81%C, 6.79%H. *Found* 41.32%C, 7.42%H.

Compound 9. $[Cp(dppe)Fe-(\eta^1-dppm)]PF_6$ 0.08 g, 0.08 mmol, γ-CD 0.2 g, 0.15 mmol. Yield 0.12 g, 54%. *Anal. Calc.* for $C_{56}H_{51}F_6P_5Fe\cdot(C_{48}H_{80}O_{40})\cdot33H_2O$. 42.46%C, 6.70%H. *Found* 42.56%C, 6.87%H.

Compound 10. $[Cp(dppe)Fe-NC-Fe(dppe)Cp]PF_6$ 0.07 g, 0.06 mmol, β-CD 0.13 g, 0.11 mmol. Yield 0.03 g. Due to the high water content good analysis data were not obtained for this compound.
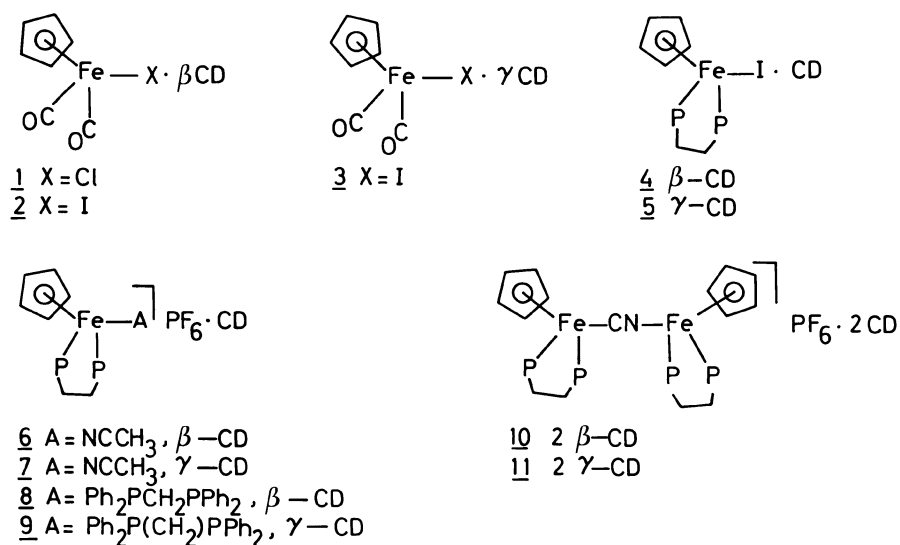
Figure 1. Schematic representation of the inclusion compounds.

Compound 11. [Cp(dppe)Fe-NC-Fe(dppe)Cp]PF$_6$ 0.1 g, 0.09 mmol, γ-CD 0.2 g, 0.15 mmol. Yield 0.05 g. Due to the high water content good analysis data were not obtained for this compound.

3. Results and Discussion

3.1. INCLUSION OF THE ORGANOMETALLIC GUEST

Inclusion compounds of the cyclopentadienyl iron complexes shown in Figure 1 were characterized by elemental analysis, and their IR, UV and ^{1}H-, ^{31}P-NMR spectra were recorded. The solid powder samples were also characterized by X-Ray diffraction and by scanning electron microscopy techniques. Stoichiometries were determined by elemental analysis and in some cases by UV-visible and ^{1}H-NMR spectroscopy. All the organometallic complexes form inclusion compounds with β- and γ-cyclodextrins but not with α-cyclodextrin. The inclusion of the binuclear complexes **10** and **11** with two β- and γ-cyclodextrins, respectively, are in agreement with previous results on other binuclear compounds [6].

The IR spectra of inclusion compounds **1–11** showed, in addition to the intense and typical bands of CD, some characteristic absorption bands of the guest; νCO for Cp(CO)$_2$FeX and νCN for [Cp(dppe)Fe-NCCH$_3$]PF$_6$, and [Cp(dppe)Fe-(μ-CN)-Fe(dppe)Cp]PF$_6$, these latter, however, were of very low intensity. Data are displayed in Table I. Thus these bands appear in a region where cyclodextrins do not absorb [20].

^{1}H-NMR spectra of the inclusion compounds exhibit in addition to the typical proton signals of the guest [6a–f] (see Table I) the signals of cyclodextrins (both β

Table I. Some spectroscopic data for the organometallic guests observed in their inclusion compounds.

Compound	IR bands (cm^{-1})	^{31}P-NMR (ppm)	^{1}H-NMR (ppm)
Cp(CO)$_2$FeCl·β-CD	2050, 2005 CO	–	5.30 Cp
Cp(CO)$_2$FeI·β-CD	2037, 1977 CO	–	5.35 Cp
Cp(CO)$_2$FeI·γ-CD	2037, 1977 CO	–	5.34 Cp
Cp(dppe)FeI·β-CD	a	112.6 dppe	7.3–7.7 C$_6$H$_5$
Cp(dppe)FeI·γ-CD	a	94.4 dppe	7.4–7.9 C$_6$H$_5$
[Cp(dppe)Fe-NCCH$_3$]PF$_6$ · β-CD	2333 CN	95.0 dppe	7.2–7.8 C$_6$H$_5$
[Cp(dppe)Fe-NCCH$_3$]PF$_6$ · γ-CD	2321 CN	b	7.3–7.9 C$_6$H$_5$
[Cp(dppe)Fe-(η^1-dppm)]PF$_6$ · β-CD	a	b	6.6–8.3 C$_6$H$_5$
[Cp(dppe)Fe-(η^1-dppm)]PF$_6$ · γ-CD	a	b	6.8–8.3 C$_6$H$_5$
[Cp(dppe)Fe-(μ-CN)-Fe(dppe)Cp]PF$_6$ · β-CD	2007 CN	101.0, 104.7 dppe −145.0, −145.9 PF$_6$	6.8–7.8 C$_6$H$_5$
[Cp(dppe)Fe-(μ-CN)-Fe(dppe)Cp]PF$_6$ · γ-CD	2007 CN	100.9, 104.7 dppe	6.8–7.9 C$_6$H$_5$

^{a} IR bands of the fragment Cp(dppe)Fe are masked by the absorptions of the CD.
^{b} Not observed.

and γ) slightly shifted upfield with respect to the free cyclodextrins. The H-3 and H-5 protons, which are located in the interior of the cyclodextrin cavity [6c,6d], undergo the most significant shift, especially H-3 which shifted 0.05–0.09 ppm upon inclusion with β cyclodextrin and 0.12–0.02 ppm with γ-cyclodextrin. These results are consistent with a shielding of the protons inside the cyclodextrin cavity of the aromatic cyclopentadienyl group of the organometallic guest.

^{31}P-NMR signals for some of the guests included in the CD host were also observed [16].

Inclusion of the organometallic guest in cyclodextrins was also confirmed by UV-visible spectroscopy in solution.

Figure 2 shows the UV-visible absorption spectrum of Cp(dppe)FeI in the absence and presence of β-CD in DMSO solution. β-CD caused a decrease of the absorption in the 429 nm region and an enhancement in the 400 nm range
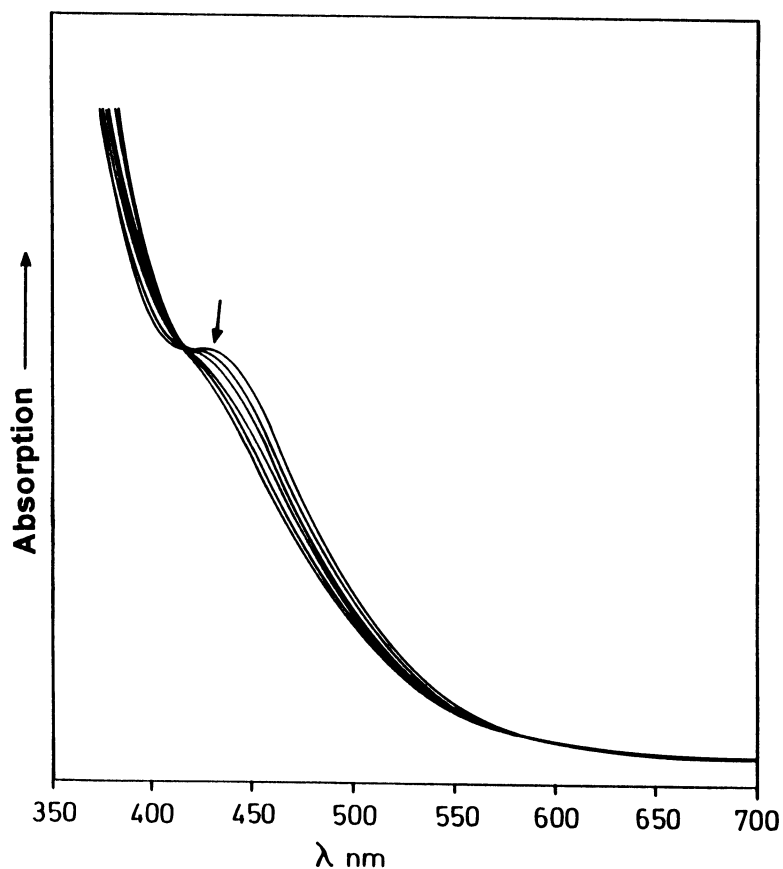
Figure 2. Electronic absorption spectra of Cp(dppe)FeI 3.56 × 10^{-3} M on addition of cyclodextrin, from 5.87 × 10^{-3} M to 2.94 × 10^{-2} M in DMSO. The arrow indicates the organometallic without cyclodextrin.

indicating the inclusion of the iron complex in the CD cavities. The isosbestic point observed at 416 nm indicates the formation of a 1 : 1 complex between CD and the organometallic complex. Thus the association constant for the 1 : 1 complex measured in DMSO according to the Hildebrand and Benesi [21] method was $K = 4.8 \times 10^{-4}$ M^{-1}

$$\text{Cp(dppe)Fe-I} + \beta\text{-CD} \rightleftharpoons \text{Cp(dppe)Fe-I} \cdot \beta\text{-CD}.$$
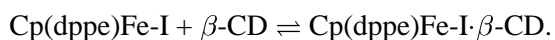
Similar results were found for Cp(dppe)FeI·γ-CD for which a K value of 1.78 × 10^{-4} M^{-1} was determined.

All the other organometallic complexes exhibited significant changes of their UV-visible absorptions on encapsulation in cyclodextrin. For instance Cp(CO)$_2$FeCl·β-CD exhibits an enhancement of the absorption maximum at 390 nm as shown in Figure 3. A similar behaviour was found for [Cp(dppe)Fe-(μ-CN)-
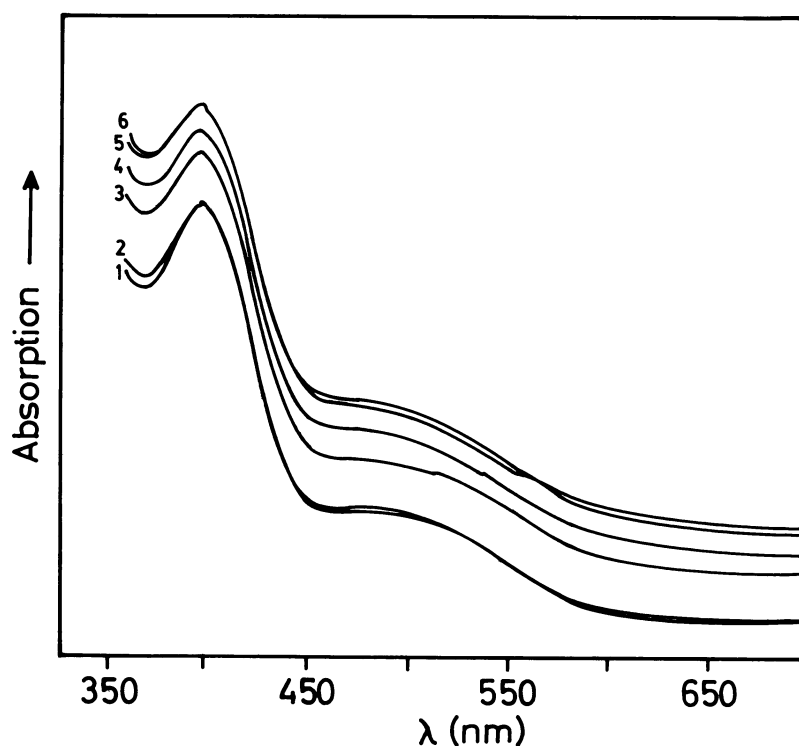
Figure 3. Spectral changes in the UV-visible spectra of CpFe(CO)$_2$Cl on inclusion in β-cyclodextrin. (1) CpFe(CO)$_2$Cl 3.0 $\times$ 10^{-3} M in H$_2$O solution. (2) (5.87 $\times$ 10^{-4} M) to (6) (2.94 $\times$ 10^{-3} M), increasing concentrations of β-cyclodextrin.

Fe(dppe)Cp]PF$_6$ · γ-CD. For the other organometallic complexes an enhancement of the absorption was observed.

The small association constant for the inclusion compounds Cp(CO)$_2$FeI·β-CD and Cp(dppe)FeI·γ-CD could be due to the bulky dppe ligands [22,23]. For ferrocene a value of $K_{\mathrm{ass}} = 50\,\mathrm{M}^{-1}$ was determined [10] and for ferrocenyl derivatives of the type (C$_5$H$_5$)Fe(C$_5$H$_4$—CH=CR—CO$_2$R$'$), R$'$ = C$_6$H$_4$NO$_2$, R = H, CH$_3$ and (R$''$HC=CH—C$_5$H$_4$)Fe(C$_5$H$_4$—CH=CR—CO$_2$R$'$), R$''$ = C(O)—OEt, values from 67 to 1200 M^{-1} have been reported [24]. Ferrocene has a ring-to-ring distance of 3.32 Å [25] while the cation Cp(dppe)Fe$^+$ exhibits a large phenyl-to-phenyl distance on the bis(diphenylphosphino)ethano molecule (ca. 7.9 Å) [22,23]. The diameters of the inner cavities of β- and γ-cyclodextrin are 7.8 and 9.5 Å, respectively. For ferrocenyl derivatives, the high association constant has been attributed to the chemical interaction between the ferrocenyl substituent and the secondary hydroxyl group of cyclodextrin [24].

Consistent with the above considerations, Cp(CO)$_2$FeCl does not form inclusion compounds with α-cyclodextrin.

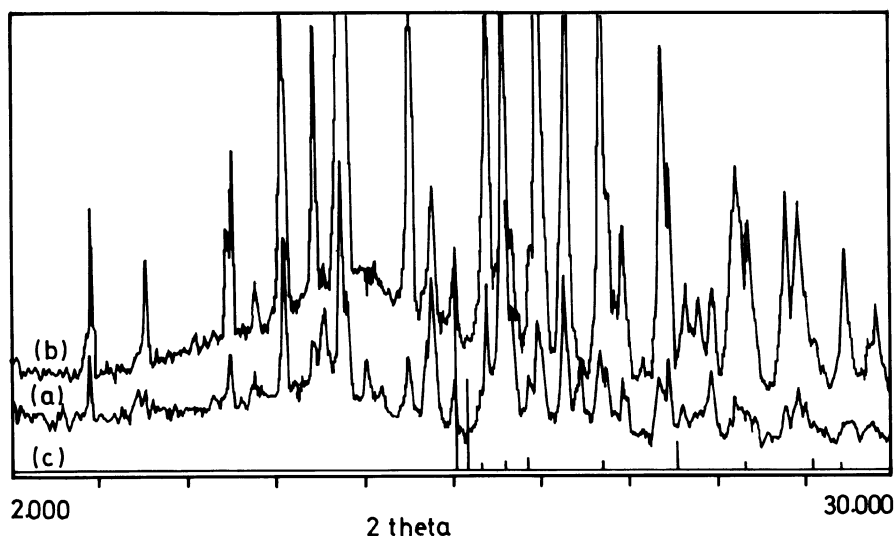*Figure 4.* X-ray powder diagram of (a) Cp(CO)$_2$FeCl·β-CD, (b) β-CD and (c) Cp(CO)$_2$FeCl.

Encapsulation of the organometallic guest in the solid state was also confirmed by X-ray powder diagrams [26]. Comparison of the X-ray diffractograms of the inclusion compounds with those of the pure components (β- or γ-CD and the organometallic guest), indicate some substantial changes in the intensity with some slight changes in the 2θ values. For instance the X-ray diagram of Cp(CO)$_2$FeCl·β-CD shown in Figure 4a reveals similar peaks to the host structure (Figure 4b) with some significant modifications of the intensity of some peaks. Peaks of the guest (Figure 4c) appear normal.

Almost all the inclusion compounds described above were obtained as microcrystalline powders. However, it should be noted that for [Cp(dppe)Fe-NCCH$_3$]PF$_6$ · γ-CD and [Cp(dppe)Fe-(η^1-dppm)]PF$_6$ · γ-CD the morphology of the solid obtained is different from that of the powder obtained with the other host–guest complexes.

For these inclusion compounds a multilayer intercalate structure was indicated by X-ray power diffraction and IR data as well as by the SEM technique. An SEM micrograph showing the morphology of the solids is presented in Figure 5. This clearly reveals the plate form of the solids. On the other hand, Figure 6 shows an SEM micrograph of the fracture edge of the plate of a sample of [Cp(dppe)Fe-NCCH$_3$]PF$_6$·γ-CD, where the shell structure of the compound is clearly observed. IR bands of compounds [Cp(dppe)Fe-NCCH$_3$]PF$_6$ · γ-CD and [Cp(dppe)Fe-(η^1-dppm)]PF$_6$ · γ-CD are similar to those of free cyclodextrin indicating no chemical modification but their X-ray powder diffraction patterns are very different to that of free cyclodextrin without guest as shown in Figure 7. This is consistent with no chemical modification of the cyclodextrin but a structural modification.
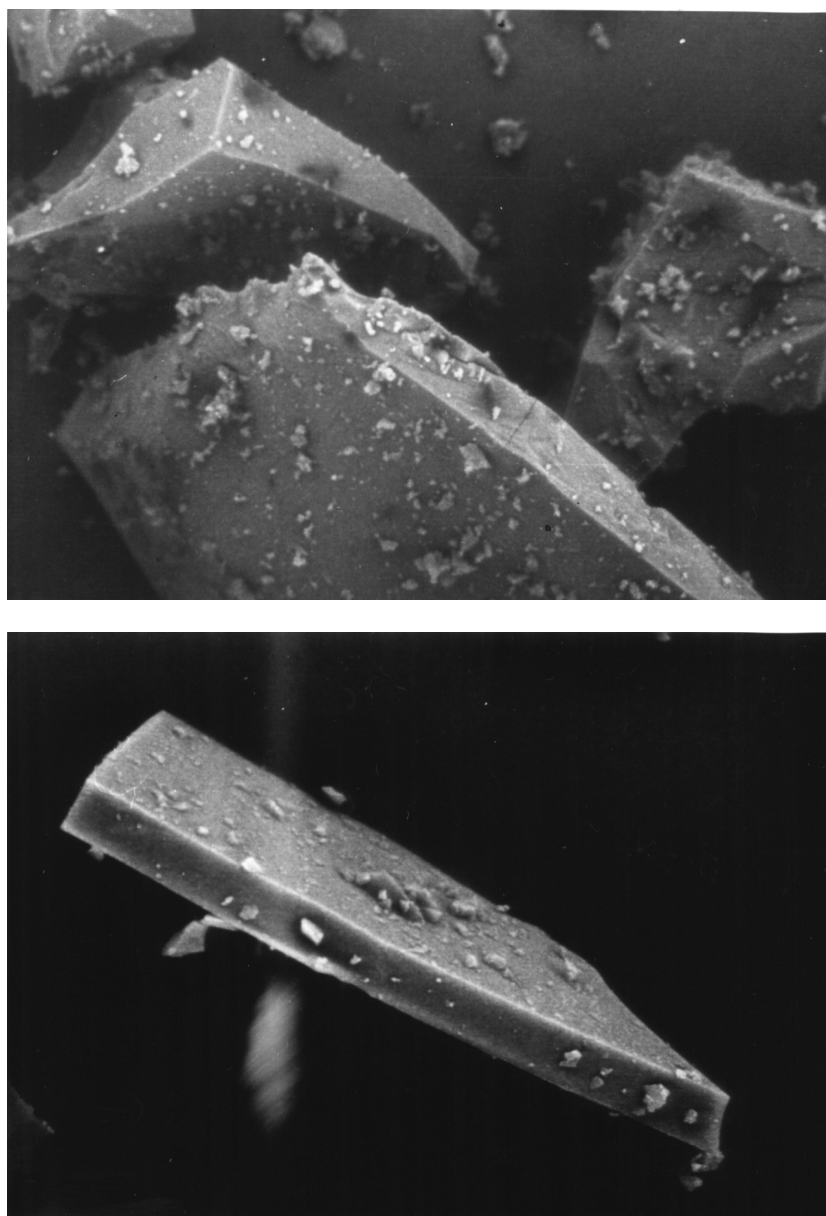
Figure 5. SEM micrograph of a plate sample of (a: upper) [Cp(dppe)Fe-NCCH$_3$]PF$_6$ · γ-CD and (b: lower) [Cp(dppe)Fe-(η^1-dppm)]PF$_6$ · γ-CD.

3.2. ENCAPSULATION EFFECT ON THE ELECTRON-TRANSFER OF THE ORGANOMETALLIC GUEST

The effect of cyclodextrin inclusion on the oxidation–reduction reactions or electron-transfer processes has not been investigated extensively [2]. We have
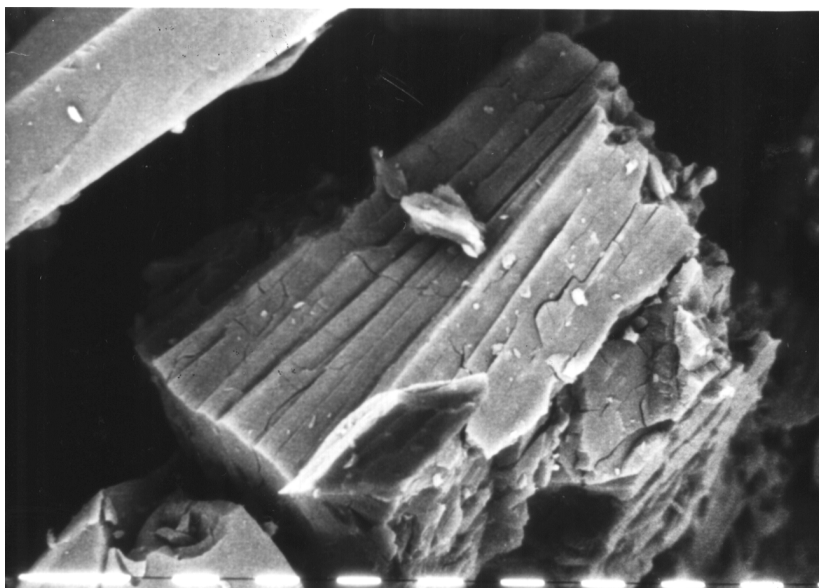
Figure 6. SEM micrograph of [Cp(dppe)Fe-NCCH$_3$]PF$_6 \cdot \gamma$-CD showing the fracture edge of a plate of the sample.

Table II. Encapsulation effect of the voltammetric data for the complex [{Cp(dppe)Fe}$_2$-μ-CN]PF$_6$.

β-CD concentration (M $\times$ 10^{-3})	E_1^0 (mV)/ΔE (mV)/ip_c/ip_a	E_2^0 (mV)/ΔE (mV)
0[a]	290/80/0.9	970/260
2.59	290/80/0.9	915/130
5.18	285/70/0.9	890/80
7.77	285/90/0.9	885/90
12.9	270/60/0.9	895/110
γ-CD concentration (M $\times$ 10^{-3})	E_1^0 (mV)/ΔE (mV)/ip_c/ip_a	E_2^0 (mV)/ΔE (mV)
0[a]	290/80/0.9	970/260
9.98	290/100/1.0	910/140
14.0	285/130/0.9	915/150
21.0	295/90/0.9	905/110

[a] Complex concentration 4.9 $\times$ 10^{-4} M in DMSO.
[b] ip_c/ip_a Cannot be measured for this wave because the proximity of a wave arising from the supporting electrolyte/DMSO system.

studied the inclusion effect on the electrochemical oxidation of Cp(dppe)FeI and the binuclear [Cp(dppe)Fe-(μ-CN)-Fe(dppe)Cp]PF$_6$ compound by cyclic voltammetry.
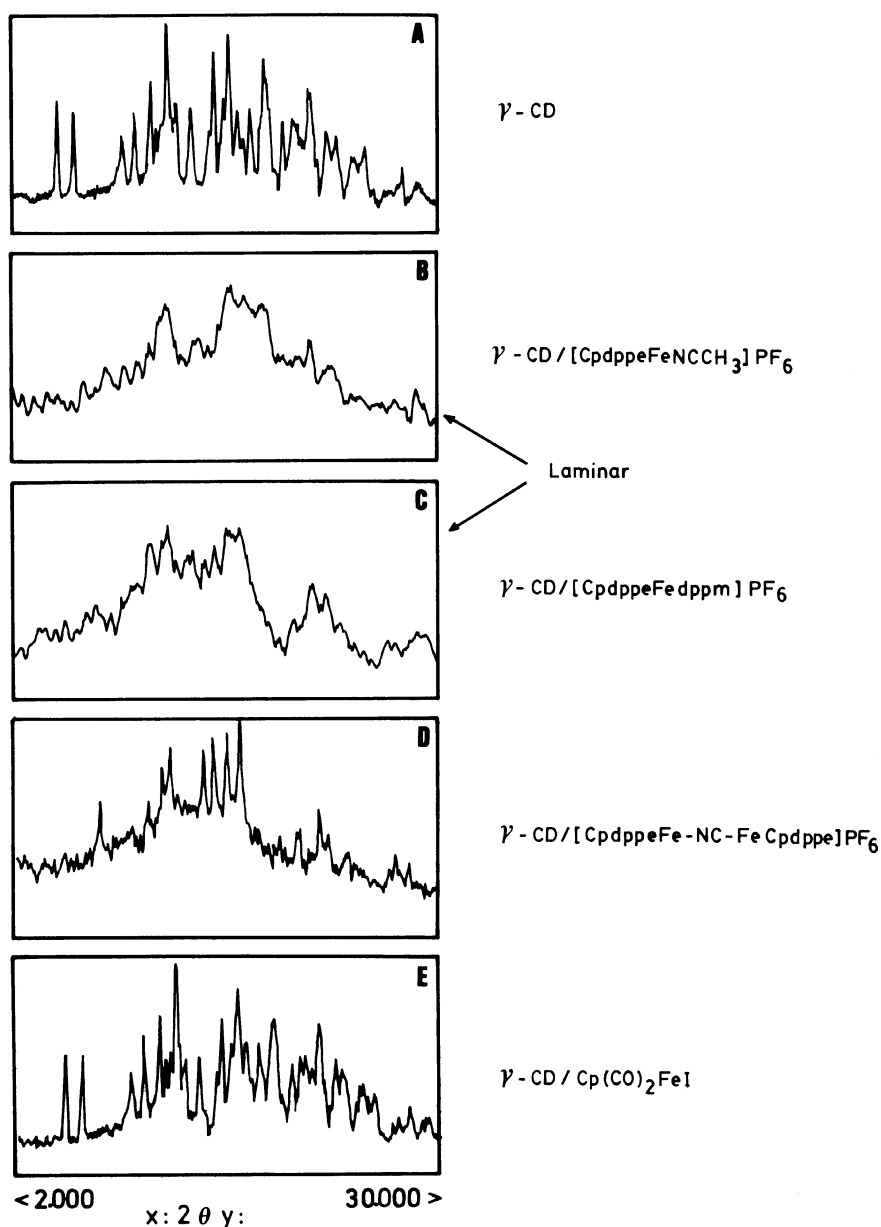
Figure 7. Powder X-ray diffractogram for (A) γ-Cyclodextrin, (B) [Cp(dppe)Fe-NCCH$_3$]PF$_6$·γ-CD, (C) [Cp(dppe)Fe-(η^1-dppm)]PF$_6$·γ-CD, (D) [Cp(dppe)Fe-NC-Fe(dppe)Cp]PF$_6$·γ-CD, (E) Cp(CO)$_2$FeI·γ-CD.

The electrochemical behavior of these complexes in CH$_2$Cl$_2$ solution has been studied previously [18a]. Because the inclusion compounds are only soluble in DMSO, we have carried out the inclusion studies in this solvent. The cyclic voltam-

Figure 8. Cyclic voltammograms 4.9×10^{-4} M in DMSO solution of [Cp(dppe)Fe-CN-Fe(dppe)Cp]PF$_6$ in the absence (A) and presence (B) of γ-CD 2.1×10^{-2} M.
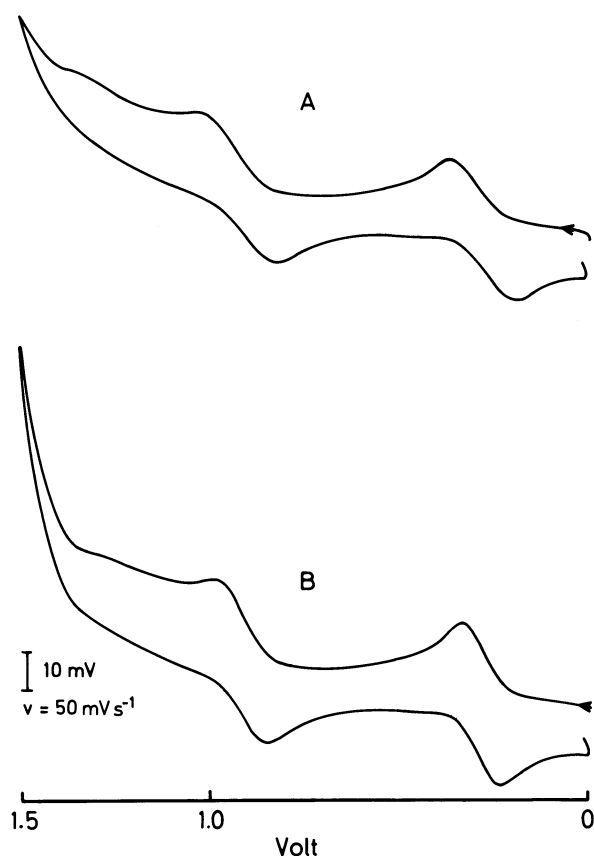
mogram of the binuclear complex in DMSO solution exhibits two oxidation waves as shown in Figure 8. According to previous studies in CH$_2$Cl$_2$ solution, the first oxidation at 0.28 V can be assigned to the electron richer N-bonded Fe moiety while the second oxidation at 0.96 V is assigned to the oxidation of the fragment Cp(dppe)FeCN. The first oxidation wave was diffusion-controlled ($i/V^{1/2}$ constant in the range 50–100 mV and chemically quasi-reversible, $I_c/I_a \approx 0.86$, ΔE_p = 0.08 V). On adding γ-cyclodextrin, as shown in Figure 8 this oxidation wave becomes reversible ($I_c/I_a = 1$) and the $E_{1/2}$ value decreases. Other data are displayed in Table II. The enhancement of the reversibility can be due to a stabilization of the cation Cp(dppe)Fe-N$^+$ on changing the environment from dimethylsulfoxide to a less reactive medium such as the cyclodextrins. The decrease of the oxidation potential on encapsulation can be explained by an enhancement of the electron density of the HOMO of the Cp(dppe)Fe-N moiety in going from dimethylsulfoxide to the cyclodextrin environment cavity. The dimethylsulfoxide solvent can act

as an acceptor through the sulfur atom, while the cyclodextrin cavity behaves as a neutral environment from the view point of donor-acceptor properties.

The second oxidation wave appears less reversible than the first ($\Delta E_p = 0.26$ V). Thus in this zone a wave characteristic of the systems DMSO/supporting electrolyte begins at about 1.6 V which preclude an estimation of the ip_c/ip_a ratio. On adding γ-cyclodextrin, similar changes to those observed for the first wave were obtained: an enhancement of the reversibility as well as a decrease of the oxidation potential.

However, it is interesting to note that the effects just described on the encapsulation do not affect both metal centers to the same extent. From Table II it can be seen that the variations on encapsulation are 0.020 V in E_1^0 and 0.07 V in ΔE_p for the first oxidation wave while for the second oxidation changes of 0.060 V in E_2^0 and 0.14 V in ΔE_p were observed. These features can be interpreted as a more efficient penetration of the cyclodextrin 'torus' by the Cp(dppe)Fe-C fragment than by the Cp(dppe)Fe-N fragment, which can be due to their different electronic density [18a,b]. Encapsulation of the binuclear complex by β-cyclodextrin produce significant changes only on the Cp(dppe)Fe-C center. Variations of 0.055 V in E_2^0 and 0.17 V in ΔE_p were observed. For the first oxidation wave only slight variations were observed (0.015 V in E_1^0 and 0.07 V in ΔE_p) which imply a weak encapsulation affect on the Cp(dppe)Fe-N center. A similar behaviour, but of greater magnitude, was observed for the γ encapsulation. This can be due to the larger cavity of γ-cyclodextrin than β-cyclodextrin. The enhancement of the oxidation peak on encapsulation by cyclodextrin has been also observed previously for ferrocenecarboxylic acid [27]. The inclusion effect on the oxidation of Cp(dppe)FeI was also investigated revealing only a small shift in the oxidation potential.

3.3. ENCAPSULATION EFFECT ON ELECTRON TRANSFER INTERVALENCE TRANSITION OF THE Fe-CN-Fe MIXED VALENCE COMPLEX

We have previously studied the intervalence transition of the mixed valence complex [{Cp(dppe)Fe}$_2$-μ-CN](PF$_6$)$_2$ in several solvents [28]. In dimethylsulfoxide solution the electron-transfer intervalence band appears around 844 nm. On adding β and γ cyclodextrin the absorptions remain almost unchanged (845 nm and 848 nm, respectively). This result was somewhat surprising, because the absorption maximum for the IT of the mixed valence complex varies considerably with the solvent as follow [28]: acetonitrile 856.5 nm, acetone 855 nm, methanol 861 nm, dichloromethane 880 nm.

This small dependence on the IT is probably due to the weak interaction between the highly charged cation [{Cp(dppe)Fe}$_2$-μ-CN]$^{++}$ and the apolar cavity of the cyclodextrin, giving no encapsulation of the cation.
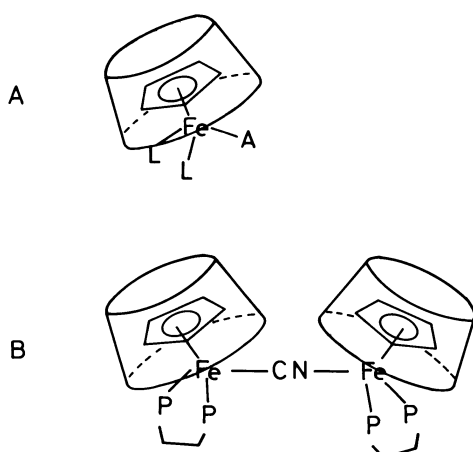
Figure 9. Schematic representation of the half-sandwich complexes. (A) Mononuclear complexes. (B) Binuclear complexes.

4. Conclusions

It has been shown that β- and γ-CD/half-sandwich inclusion complexes are obtained by coprecipitation from the interface of water/CH_2Cl_2 solvents. The $1:1$ stoichiometry for the inclusion compound containing mononuclear organometallic complexes as well as the $2:1$ cyclodextrin/organometallics stoichiometry for the inclusion compounds containing the binuclear complexes agree well with the composition found for the inclusion compound with similar mononuclear [3,5,11] and binuclear organometallics guests [3,6] (see Figure 9). Inclusion compounds containing the bulky dppe produces a partial inclusion of the organometallic guest giving low association constants. The compounds [Cp(dppe)Fe-NCCH$_3$]PF$_6$ · γ-CD and [Cp(dppe)Fe-(η^1-dppm)]PF$_6$ · γ-CD exhibit an unsual laminar structure, to our knowledge the only examples of cyclodextrins having a layered structure [29]. This particular type of structure is apparently induced by some peculiar characteristics of the organometallics guest [Cp(dppe)Fe-NCCH$_3$]PF$_6$ and [Cp(dppe)Fe-(η^1-dppm)]PF$_6$, about which we are not yet clear. Thus the structural consequences of varying the guest geometry has led to several types of inclusion compounds: channel-type structures [5], molecular necklace-type structures [30] and molecular nanotube-type structures [31].

Experiments considering the electron-transfer in the laminar compounds in the solid state are in progress.

Encapsulation of both β and γ cyclodextrin produces significant changes in the oxidation processes of the two metallic fragments, confirming the $2:1$ host–guest stoichiometry proposed for compounds **10** and **11**. It appears that cyclodextrins act as second coordination spheres, like an apolar solvent in the electron transfer processes.

Acknowledgements

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