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Inclusion complex formation of diferrocenyldimethylsilane with β-cyclodextrin

José A. Fernandes [a], Sérgio Lima [a], Susana S. Braga [a], Paulo Ribeiro-Claro [a,*], José E. Rodriguez-Borges [b], Cátia Teixeira [b], Martyn Pillinger [a], José J.C. Teixeira-Dias [a], Isabel S. Gonçalves [a,*]

[a] Department of Chemistry, CICECO, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal
[b] CIQ, Department of Chemistry, University of Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal

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Abstract

An inclusion compound comprising β-cyclodextrin (β-CD) and diferrocenyldimethylsilane, Fc–$SiMe_2$–Fc [Fc = (η^5-C_5H_5)Fe(η^5-C_5H_4)], has been prepared and characterized in the solid state by powder X-ray diffraction (XRD), thermogravimetric analysis (TGA) and magic angle spinning (MAS) NMR spectroscopy (^{13}C, ^{29}Si). Elemental analysis indicated that the host:guest molar ratio in the product was approximately 1.5. Ab initio calculations in vacuo were carried out in order to investigate the possible inclusion modes. The first structure, designated form **2a**, was determined assuming a barrel-type conformation, with parallel head-to-head cyclodextrins. A second V-shaped complex (**2b**) was also found by allowing variation of the angle between the cyclodextrins. Form **2a** was assumed to be the best approximation to the real structure, since this geometrical arrangement favors the formation of a channel-type packing motif.

Keywords: β-Cyclodextrin; Inclusion compounds; Host–guest systems; Oligo(ferrocenes); Ferrocene; Ab initio calculations

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides comprising six (α-CD), seven (β-CD), eight (γ-CD) and more D-glucose units linked by α-(1 → 4) glycosidic bonds [1–3]. Their shape is like a hollow truncated cone. A wide range of organic molecules, inorganic ions and metallo-organic species form inclusion complexes with CDs [3–5]. Suitable guests include transition metal complexes and organometallic compounds bearing hydrophobic ligands such as cyclopentadienyl (Cp = η^5-C_5H_5) and η^6-arene groups [5–7]. With these ligands, the weaker categories of non-covalent bonding, such as van der Waals and charge transfer interactions, assume considerable importance. Encapsulated metallo-organic complexes often exhibit markedly different physical and chemical characteristics compared to the bulk material [8], for example, in their non-linear optical [9], photophysical [10] and electrochemical properties [11], and ligand substitution/insertion reactions [12]. Cyclodextrins are known to bind ferrocene and its derivatives [11b,11c,11d,11e,13], metallocene dihalides [14], aromatic ruthenium complexes [15], mixed sandwich complexes such as [(η^5-C_5H_5)Fe(η^6-C_6H_6)](PF_6) [16], and various half-sandwich metal carbonyl and cyano complexes [17]. Inclusion compounds containing 4-ferrocenylpyridine methyltrioxorhenium and ferrocenyldiimine metal carbonyl complexes have also been reported [18]. The difficulty in obtaining high quality single crystals suitable for X-ray diffraction (XRD) has

* Corresponding authors. Tel.: +351 234 378190; fax: +351 234 370084.
E-mail address: igoncalves@dq.ua.pt (I.S. Gonçalves).

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meant that only a few solid-state structures have been fully determined for CD inclusion compounds containing metallo-organic complexes. Nevertheless, full characterization using other methods such as powder XRD and NMR can provide important structural information [19–21]. Molecular modeling calculations also help to investigate host–guest interactions and predict possible binding modes [21–27]. Herein, we present an experimental and theoretical study of the encapsulation of diferrocenyldimethylsilane by β-cyclodextrin. Diferrocenyldimethylsilane is the first member of a series of linear oligo(ferrocenyldimethylsilanes) with the general formula $FcSiMe_2[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4SiMe_2)]_nFc$ [Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$, $n = 0$–7], which can be prepared by the anionic ring-opening oligomerization of the silicon-bridged [1]ferrocenophane $Fe(\eta^5\text{-}C_5H_4)_2SiMe_2$ [28]. These oligo(ferrocenes) have attracted attention with respect to their electrochemical, electronic and magnetic properties, and they are also models for the corresponding poly(ferrocenylsilane) high polymers [29].

2. Experimental

2.1. Materials and methods

All air-sensitive reactions and manipulations were performed using standard Schlenk techniques under an oxygen-free and water-free argon atmosphere. Solvents were dried by standard procedures (*n*-hexane over Na/benzophenone ketyl and CH_2Cl_2 over CaH_2), distilled under argon and kept over 4 Å molecular sieves. β-CD (Fluka) and ferrocene (Aldrich) were obtained from commercial sources and used as received. Monolithioferrocene was prepared according to the literature procedure [30].

Microanalyses for CHN were performed at the ITQB, Oeiras, Portugal (by C. Almeida), and Fe was determined by ICP-OES at the Central Laboratory for Analysis, University of Aveiro (by E. Soares). Powder XRD data were collected on a Philips X'pert diffractometer using Cu Kα radiation filtered by Ni ($\lambda = 1.5418$ Å). TGA studies were performed using a Mettler TA3000 system at a heating rate of 5 K min^{-1} under a static atmosphere of air. Infrared spectra were recorded on a Unican Mattson Model 7000 FT-IR spectrophotometer using KBr pellets. ^1H NMR spectra were measured in solution using a Bruker CXP 300 spectrometer. Solid-state ^{13}C and ^{29}Si CP MAS NMR spectra were recorded at 100.62 and 79.49 MHz, respectively, on a (9.4 T) Bruker Avance MSL 400P spectrometer. ^{13}C CP MAS NMR spectra were recorded with 4.5 μs ^1H 90° pulses, 1.0 ms contact time, a spinning rate of 5.0 kHz and 4 s recycle delays. ^{29}Si CP MAS NMR spectra were recorded with 5 μs ^1H 40° pulses, 5.0 ms contact time, a spinning rate of 5.0 kHz and 5 s recycle delays. Chemical shifts are quoted in parts per million from TMS.

2.2. Preparation of (1,1′-ferrocenediyl)dimethylsilane

A mixture of ferrocene (20 g, 108 mmol), *n*-butyl-lithium (99 mL, 2.5 M), *n*-hexane (135 mL) and tetramethylethylenediamine (20 mL) was stirred at 0 °C for 16 h. The resulting yellow solid was isolated by filtration and washed several times with anhydrous *n*-hexane (31 g, 90%). This product (31 g, ca. 97 mmol) was mixed with Cl_2SiMe_2 (10.25 mL) and *n*-hexane (365 mL), and left stirring overnight at 0 °C. The solvent and the unreacted dichlorodimethylsilane were removed under vacuum to obtain an orange solid. This product was washed several times with anhydrous *n*-hexane to isolate (1,1′-ferrocenediyl)dimethylsilane (15.4 g, 66%).

2.3. Diferrocenyldimethylsilane (*1*)

Following the literature method [28,31], a mixture of ferrocenylsilane oligomers was obtained from the reaction of (1,1′-ferrocenediyl)dimethylsilane with monolithioferrocene. The mixture was fractionated using an alumina chromatographic column (90 active, acidic [Activity I] Merck 0.063–0.200 mm, 70–230 mesh ASTM) and a 9:1 hexane/dichloromethane mixture as the mobile phase. Fractions of 250 mL were collected, the first six containing pure ferrocene. Fractions 7–19, containing a mixture of ferrocene and the dimer **1**, were submitted to a second chromatography using neutral alumina (Typ. 507C Brockmann I, STD grade, Approx. 150 Mesh, 58 Å) and the same mobile phase to yield 2.6 g of pure diferrocenyldimethylsilane (**1**). Fractions 20–39 of the first chromatography contained ferrocene, compound **1** and the trimer 1,1′-bis(ferrocenyldimethylsilyl)ferrocene, and were separated in another chromatography with neutral alumina to yield 0.33 g of **1**. The total amount of compound **1** obtained was therefore 2.93 g.

2.4. Reaction of β-CD with diferrocenyldimethylsilane (β-CD/*1*)

A solution of diferrocenyldimethylsilane (**1**) (20.0 mg, 0.047 mmol) in ethanol (2.0 mL) was added to a solution of β-CD (122.8 mg, 0.094 mmol) in water (3.0 mL) at 60 °C. A yellow suspension formed immediately, which turned paler after stirring for 4 h. The pale yellow solid was isolated by centrifugation and washed with water (2×5 mL). Yield: 100 mg. Anal. Calc. for $2(C_{42}H_{70}O_{35}) \cdot 1.3(C_{22}SiH_{24}Fe_2) \cdot 17H_2O$ (3132.9): C, 43.17; H, 6.60; Fe, 4.63. Found: C, 43.27; H, 7.22; Fe, 4.64. IR (KBr, cm^{-1}): $\nu = 3371$ s, 2929 m, 1643 m, 1422 m, 1371 m, 1334 m, 1304 m, 1248 m, 1203 m, 1157 s, 1099 sh, 1080 s, 1053 sh, 1028 vs, 1002 s, 938 m, 861

m, 842 w, 819 m, 797 m, 756 m, 704 m, 682 w, 668 s, 653 w, 608 m, 577 m, 529 m, 503 w, 483 w, 451 m, 356 w. ^{13}C CP MAS NMR: $\delta = 104.0$ (β-CD, C_1), 82.3, 80.6 (β-CD, C_4), 72.8 (β-CD, $C_{2,3,5}$), 68.9 (Cp), 60.8 (β-CD, C_6), 1.0, −0.2, −1.0, −1.6 ($SiMe_2$) ppm. ^{29}Si CP MAS NMR: $\delta = -7.0$ ppm ($SiMe_2$).

2.5. Ab initio calculations

Ab initio calculations were carried out using the Gaussian 03W program package, running on a personal computer [32]. Compound **1** was fully optimized at the B3LYP/LanL2DZ level. Several conformers are possible due to rotation about the $C_{(ring)}$–Si bonds. In addition, the internal rotation of cyclopentadienyl rings about the principal axes of the ferrocene units allows the existence of eclipsed and staggered conformations. In ferrocene, the eclipsed (D_{5h}) form was found to be more stable than the staggered (D_{5d}) form by 2.78 kJ mol^{-1} [33]. Molecular mechanics (MM) studies of the dimer **1** were reported by Barlow et al. [34]. For the sake of comparison, we will use their terminology for the two dihedral angles Fe–$C_{(ring)}$–Si–$C_{(ring)}$, ϕ and ψ, which define the relative disposition of the two ferrocene units. The MM calculations performed by Barlow et al. gave the lowest energy global minimum at $\phi = 36°$, $\psi = 162°$ and the next minimum 4.2 kJ mol^{-1} higher at $\phi = \psi = 70°$. The third minimum, 16.3 kJ mol^{-1} higher than the global minimum, was found at $\phi = \psi = 167°$. The ab initio calculations carried out in the present work do not agree with these MM results, concerning both the geometry and the energy of the minima. Thus, three different isomers of **1** were found, with an energetic difference of only 1.5 kJ mol^{-1} and a rotational barrier of 16 kJ mol^{-1} between them (Fig. 1). The pair of conformers with $\phi = \pm 66°$ and $\psi = 179°$ correspond to the lowest energy, but their geometry is not suitable for inclusion in head-to-head β-CD dimers (which, on the basis of the characterization data for the sample β-CD/**1**, are the likely species present in the inclusion compound). The other conformer, with $\phi = \psi = 179°$ (i.e., close to the idealized $\phi = \psi = 180°$ conformation) was chosen as the guest for inclusion, given its higher symmetry and low energy difference relative to the absolute minimum (the in-vacuum value of ca. 1.5 kJ mol^{-1} can easily be overcome by intermolecular interactions in the solid).

The models of the inclusion complexes were obtained by single point scanning calculations, using the two-layer approximation of Morokuma and co-workers [35], with the organometallic guest treated at high layer (B3LYP/LanL2DZ) and the cyclodextrin host set as low layer (HF/CEP-4G). The host molecule was created using the crystallographic data for a β-CD · *p*-hydroxybenzaldehyde inclusion complex [36]. Two different β-CD · diferrocenyldimethylsilane geometries were calculated,

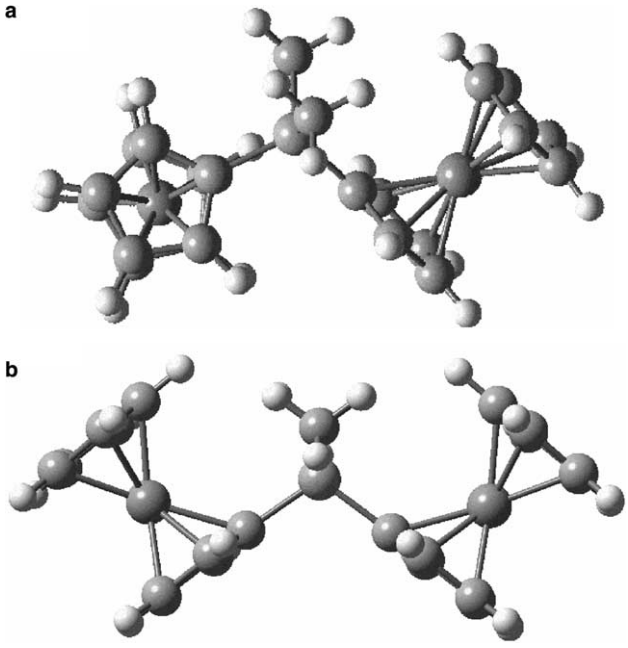

Fig. 1. (a) The lowest ($\phi = \pm 66°$ and $\psi = 179°$) and (b) second lowest ($\phi = \psi = 179°$) energy conformations of **1**, as determined by ab initio calculations.

based on a head-to-head dimer configuration with a 2:1 (host-to-guest) stoichiometry. The optimization through single point calculations was used due to the failure of the built-in optimization procedures to converge to a stable geometry under the ONIOM conditions. The scanning was performed on a 30 pm/5° grid for the r, Δh, θ, φ and γ coordinates (see Fig. 2 for the definition of these coordinates). The minimum energy structures were determined from quadratic interpolation, using the lowest energy points in the grid. A word of caution is required concerning the calculated energy values, as they are not corrected for basis set superposition error (BSSE) or for zero point vibrational energy. The BSSE correction is not available for ONIOM calculations and frequency calculations only apply to fully optimized structures.

3. Results and discussion

3.1. Synthesis and characterization of the β-CD · diferrocenyldimethylsilane inclusion compound

A solution of diferrocenyldimethylsilane (**1**) in ethanol was added to an aqueous solution of β-CD to form a thin yellow suspension that became paler as the inclusion compound was formed. The product (β-CD/**1**) was isolated by centrifugation and washed with water. Elemental analysis indicated that the β-CD:diferrocenyldimethylsilane molar ratio in the product was approximately 1.5. Since powder XRD, TGA and ^{29}Si

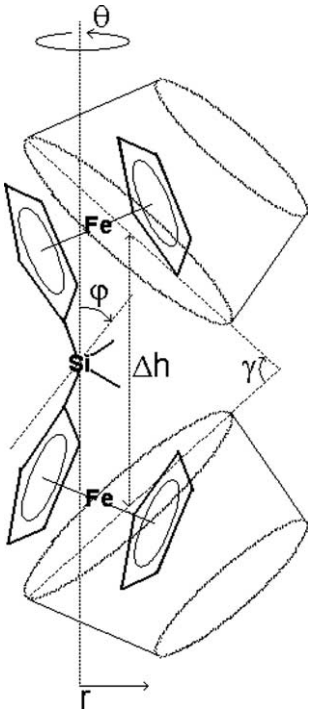

Fig. 2. Coordinate system used in the single point scanning calculations.

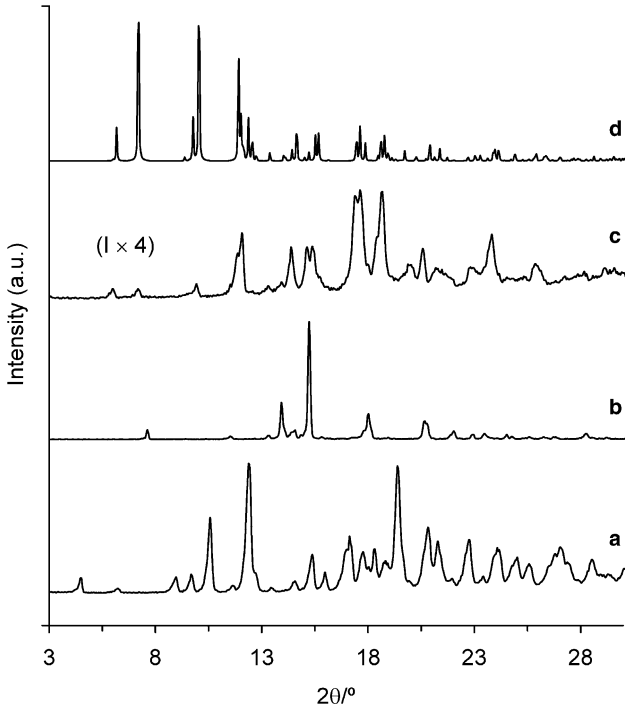

Fig. 3. Experimental (a–c) and simulated (d) powder XRD patterns of plain β-CD hydrate (a), compound **1** (b), the sample β-CD/**1** (c), and the 1:1 complex of β-CD with benzocaine [37] (guest molecules omitted from the simulation for simplicity).

MAS NMR data did not reveal the presence of bulk **1** in the product (see below), the elemental analysis can be explained by the formation of a 2:1 (host:guest) complex (hereafter referred to as **2**) mixed with a small amount of a 1:1 complex, or perhaps even a 2:1 complex with additional diferrocenyldimethylsilane molecules located at interstitial positions between the macrocycles. Fig. 3 shows the powder XRD patterns for pristine β-CD hydrate, the oligo(ferrocenylsilane) **1** and the sample β-CD/**1**. The powder XRD pattern of the sample β-CD/**1** does not contain peaks corresponding to pristine β-CD hydrate or compound **1**, and in fact shows several new peaks which indicate the formation of a new crystalline phase. This is an initial indication for the formation of a true inclusion complex [4]. Fig. 3 also shows a diffraction pattern calculated using the crystal structure data for the 1:1 β-CD inclusion compound of ethyl 4-aminobenzoate (benzocaine) [37]. This compound exhibits the typical channel-type structure consisting of head-to-head dimers of β-CD molecules stacked along the crystallographic c-axis. β-CD's frequently crystallize as face-to-face dimers when including moderate-to-large size molecules. Such β-CD dimers have been observed to pack in up to six different modes [1,2,38,39], the most common of which is where the β-CD molecules are stacked along the crystallographic c-axis, in an alternating head-to-head and tail-to-tail channel mode. Caira [19] showed that, in general, within an isostructural series of CD inclusion complexes, the gross features of the powder diffraction patterns are constant, regardless of the nature of the included guest. Although there are substantial differences between the experimental and simulated patterns shown in Fig. 3, it is evident that both patterns have peaks centered around 6.1°, 7.2°, 9.9°, 12.0°, 17.6° and 18.7° 2θ, and we may therefore tentatively assume channel-type packing for the CD molecules in β-CD/**1**.

TGA was performed on pure β-CD hydrate, the sample β-CD/**1** and a 2:1 physical mixture of β-CD and diferrocenyldimethylsilane (**1**) (Fig. 4). The physical mixture exhibits two separate weight losses which correspond to the zones where compound **1** sublimes (160–265 °C), and β-CD melts and decomposes (280–340 °C). The trace for the sample β-CD/**1** is very different in that decomposition only begins at about 260 °C. There is no identifiable step below this temperature characteristic of non-included **1**. These results indicate that the thermal behavior of the greater part of the organometallic species present has been modified by inclusion in β-CD [17e]. This conclusion is also supported by the low temperature thermal behavior. Thus, TGA of β-CD shows a well-defined step from room temperature up to about 120 °C, assigned to removal of water molecules located in the β-CD cavities, and also in the interstices between the macrocycles (14.2%, 10–11 water molecules per β-CD molecule). The corresponding dehydration profile for the sample β-CD/**1** is different and extends over a much wider range (25–150 °C), although the weight loss is less (8.5%). The lower water content

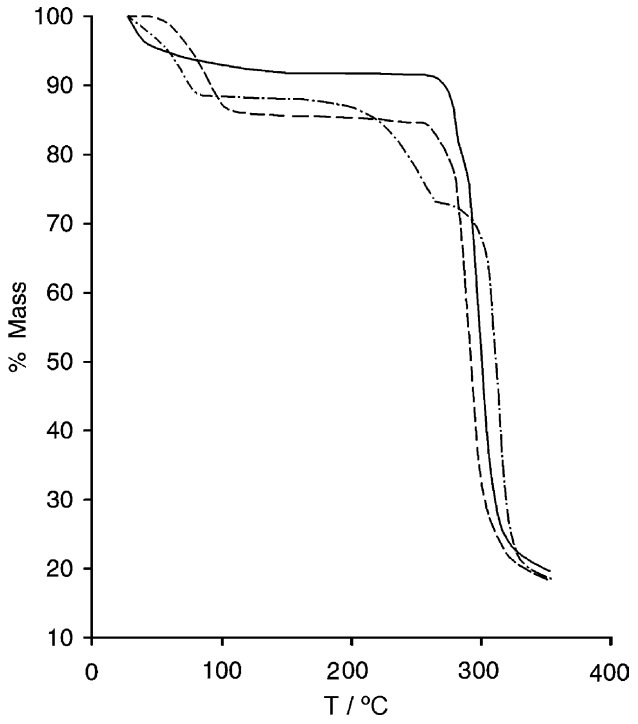

Fig. 4. Thermogravimetric profiles of plain β-CD hydrate (– – – –), a 2:1 physical mixture of β-CD and diferrocenyldimethylsilane (**1**) (– · – · –) and the sample β-CD/**1** (——).

is in reasonable agreement with elemental analysis, suggesting about 8 water molecules per β-CD molecule. The reduction in the number of water molecules per β-CD molecule is consistent with at least partial occupation of the β-CD cavity by the organometallic guest.

Fig. 5 shows the solid-state ^{13}C CP MAS NMR spectra of β-CD hydrate, diferrocenyldimethylsilane (**1**) and the sample β-CD/**1**. The spectrum of β-CD hydrate is similar to that previously reported and exhibits multiple resonances for each type of carbon atom [40]. This has been mainly correlated with different torsion angles about the (1 → 4) linkages for C_1 and C_4 [40a,40b], and with torsion angles describing the orientation of the hydroxyl groups [40c]. The different carbon resonances are assigned to C_1 (101–104 ppm), C_4 (78–84 ppm), $C_{2,3,5}$ (71–76 ppm) and C_6 (57–65 ppm). The spectrum of compound **1** shows single peaks for the Cp (η^5-C_5H_5) and methyl groups at about 69 and 1 ppm, respectively. Several weaker signals in the range 70–77 ppm are assigned to the carbon atoms of substituted cyclopentadienyl rings. The multiplicities in the resonances for the β-CD carbon atoms are reduced in the spectrum of β-CD/**1**, giving broader signals with much less structure, if any, thus suggesting a symmetry increase for the β-CD macrocycle upon inclusion. In contrast, in the region of the methyl group resonances, several overlapping peaks are observed between −2 and 0 ppm. These are attributed to encapsulated diferrocenylsilane molecules that are in different environments. A single peak is present

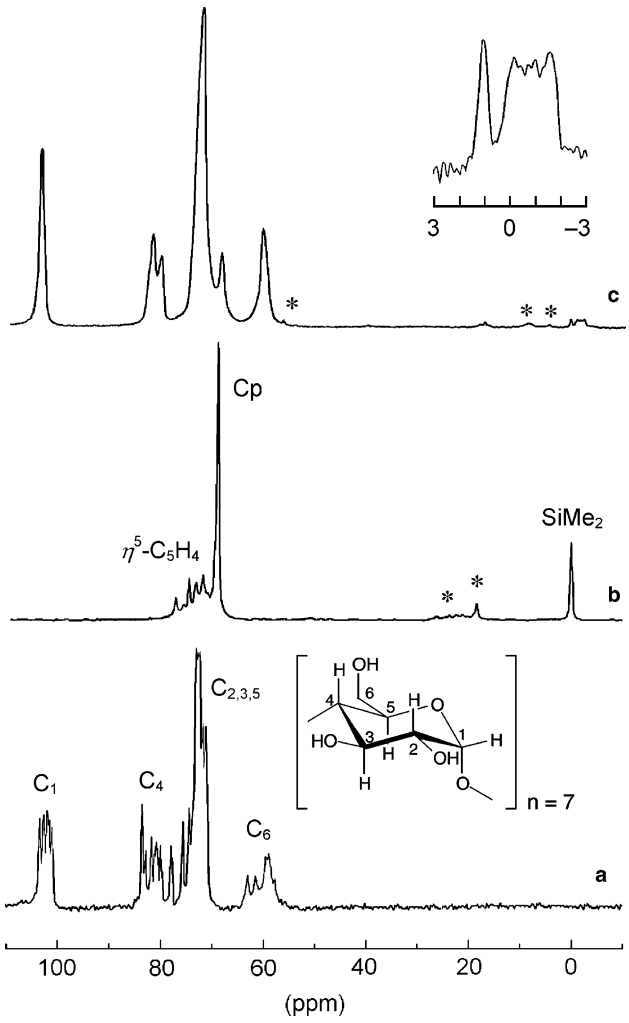

Fig. 5. Solid-state ^{13}C CP MAS NMR spectra of (a) plain β-CD hydrate, (b) diferrocenyldimethylsilane (**1**), and (c) the sample β-CD/**1**. Spinning sidebands are denoted by asterisks.

at about 69 ppm for the Cp carbon atoms. ^{29}Si CP MAS NMR spectra were also recorded for the dimer **1** and β-CD/**1** (not shown). Crystalline **1** exhibits one peak for the bridging dimethylsilyl group at about −5.3 ppm. A single slightly broader peak was observed for β-CD/**1** at −7.0 ppm. The shift to higher field is probably due to differences in the bulk susceptibility of the compounds **1** and β-CD/**1**. The absence of a peak at −5.3 ppm in the spectrum of β-CD/**1** confirms that the sample did not contain non-included **1**.

3.2. Ab initio calculations

Two different inclusion modes were calculated for the adduct **2** comprising two β-CD molecules and one diferrocenyldimethylsilane molecule (Table 1, Fig. 6). One of these, form **2a**, was determined assuming a barrel-type conformation, with parallel cyclodextrin hosts. The V-shaped form **2b** was determined by allowing variation

of the angle between the cyclodextrins. The calculated inclusion energies are −100 kJ mol^{-1} for **2b** and −81 kJ mol^{-1} for **2a**. These values are comparable with the inclusion energy of ca. −70 kJ mol^{-1} obtained for the 1:1 β-CD · ferrocene adduct, using the same calculation scheme (see computational details).

The reliability of the inclusion geometries obtained at different computational levels has recently been assessed by Casadesús et al. [41], based on the occurrence of unrealistic H···H host–guest contacts. Both of the structures **2a** and **2b** present two H···H contacts that are in the 188–200 pm range. Nevertheless, according to Casadesús et al. [41], we may assume that the calculated structures are plausible, since only a few distances are below 220 pm. On the other hand, the presence of such short contacts shows that a significantly deeper inclusion of the guest in the CD cavity is not possible.

The presence of intermolecular hydrogen bonds, host–guest, host–host or guest–guest, is known to play an important role in the stabilization of CD inclusion complexes [23a,23b,42]. Both of the calculated structures **2a** and **2b** present some short contact interactions between the hydrogen atoms of the guest cyclopentadienyl groups and the oxygen atoms of β-CD. These short contacts, which are within the 224–235 pm range for **2a**, and within the 266–298 pm range for **2b**, fall in the expected range for C–H···O interactions, and are likely to contribute to the stability of the complex [42].

A different situation arises concerning the intermolecular bonds between the two β-CD rims, which are expected to contribute to the stabilization of β-CD dimers [23a,23b]. For a direct interaction, the O···O distance between the two cyclodextrins ($O_{CD} \cdots O_{CD'}$) must be less than about 350 pm [43]. Both of the structures **2a** and **2b** present $O_{CD} \cdots O_{CD'}$ distances above this minimum value. The shortest $O_{CD} \cdots O_{CD'}$ distances are found for structure **2b** (380 pm < $O_{CD} \cdots O_{CD'}$ < 1000 pm). For the barrel-shaped structure **2a**, the inter-CD distance $O_{CD} \cdots O_{CD'}$ is 580 pm, much too long to allow a direct bonding between the β-CD units. However, 580 pm is a reasonable distance to fit bridging water molecules, which could form indirect hydrogen bonds [43]. As a result, a larger β-CD dimer cavity would be formed, fully accommodating the guest molecule.

Although the results of the theoretical calculations provide a limited interpretation of the solid-state inclusion compound, as the effects of hydration water and molecular packing were not included in the calculations, they still provide insight into the influence of the guest and the β-CD host on the structure of the complex unit. In an isolated and dehydrated complex unit, the V-shaped guest would force the β-CD molecules to align their cavity axes with those of the ferrocenyl units, yielding a V-shaped structure (form **2b**). A similar structure was recently found by molecular dynamics simulations of a solvated 2:1 γ-CD:C_{60} inclusion complex [23c]. However, this geometrical arrangement is unusual and, to the best of our knowledge, has never been observed in crystallographic studies of CD inclusion compounds. The solid-state experimental data for the sample β-CD/**1** suggest that the inclusion complex **2** has the common channel-type structure, which probably means that the host molecules are arranged as parallel head-to-head dimers engulfing the guest (form **2a**). The calculations clearly show that this geometry does not allow a direct contact between the wider CD rims in the CD dimer. However, the inter-CD distance is long enough to accommodate water molecules and the dimer structure could be stabilized by indirect $O_{CD} \cdots O_{water} \cdots O_{CD'}$ hydrogen bonds.

Table 1
Calculated values by single point scanning

Adduct	r_{Si} (pm)	Δh (pm)	γ (°)	φ (°)	E (kJ mol^{-1})
2a	30	330	Set = 0	0	−81
2b	40	420	33	Set = 0	−100

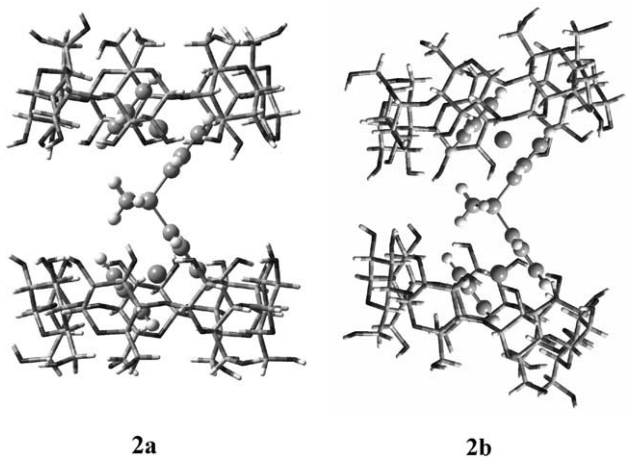

Fig. 6. Calculated structures for the inclusion complex **2** comprising a β-CD dimer encapsulating diferrocenyldimethylsilane (**1**).

4. Concluding remarks

The experimental and theoretical study presented here has demonstrated that β-cyclodextrin forms an inclusion complex with diferrocenyldimethylsilane (**1**). As noted in the introduction, the dimer **1** is the first member of a series of linear oligo(ferrocenyldimethylsilanes), which are models for the corresponding poly(ferrocenylsilane) high polymers. We are currently investigating the interactions of these oligomers and polymers with cyclodextrins, with the intriguing possibility of obtaining hybrid organic-organometallic pseudo-(poly)rotaxane structures.

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