Inclusion Complexation of Dimeric and Trimeric Oligo(ferrocenyldimethylsilanes) with γ-Cyclodextrin

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Received July 29, 2005

The oligo(ferrocenyldimethylsilanes) $FcSiMe_2Fc$ and $FcSiMe_2[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4SiMe_2)]$-Fc [$Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$] were encapsulated in γ-cyclodextrin (CD) to give crystalline inclusion compounds with 2:1 and 3:1 (host-to-guest) stoichiometries, respectively. A complex between γ-CD and ferrocene was also prepared for comparison. The formation of true inclusion complexes was confirmed in the solid state by powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), and $^{13}C/^{29}Si$ CP MAS NMR spectroscopy. Powder XRD reveals that the complexes containing ferrocene and the trimer 1,1′-bis(ferrocenyldimethylsilyl)ferrocene have very similar solid-state structures based on channel-type packing of the host molecules. The complexes containing the oligo(ferrocenyldimethylsilanes) dehydrate up to 100 °C, after which no mass loss is registered by TGA in the temperature range 100−225 °C. The dissociation of the complexes occurs slightly above 225 °C and is immediately followed by the simultaneous release of the guests and the decomposition of the host in the temperature range 250−310 °C. ^{13}C CP MAS NMR spectra of the inclusion compounds show that the encapsulation of the guest molecules in the CD cavity induces the host macrocycle to adopt a more symmetrical conformation, with each glucose unit in a more similar environment. The inclusion modes are discussed.

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, and they have no hydroxy groups inside their cavity. Although the depths of the cavities for the three CD molecules are the same (7.9 Å), their cavity diameters are different: ca. 5.7, 7.8, and 9.5 Å for α-, β-, and γ-CD, respectively. CDs are known to form inclusion complexes with a large number of low molecular weight organic molecules, inorganic ions, and metallo-organic species.[3−5] Since the early 1990s, the interaction of CDs with organic polymers has also been extensively investigated.[6−12] Examples of polymers that have been suc-

cessfully encapsulated include poly(propylene glycol), polypropylene, poly(methyl vinyl ether), polyisobutylene, polyesters, and polyamines. The resultant inclusion complexes are main-chain polyrotaxanes, which are potentially of interest as molecular machines.[12] Within this field, inorganic polymers have started to attract attention because they have excellent features such as resistance to heat and certain chemicals. Harada and co-workers have studied silicon-containing polymers and have shown that β- and γ-CD form inclusion complexes with poly(dimethylsiloxanes) and poly(dimethylsilanes) of various molecular weights to give crystalline compounds.[13]

A further, largely unexplored, approach for the formation of cyclodextrin-based supramolecular architec-

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tures is to use main-chain organometallic polymers as the guest. Considering that ferrocene and its derivatives are ideal guests for CDs,[14] we have started to explore the possibility of encapsulating oligomers and polymers that contain ferrocene units in the main chain, namely, oligo(ferrocenylsilanes) and poly(ferrocenylsilanes). Poly-(ferrocenyldimethylsilane), for example, is available through the ring-opening polymerization (ROP) of the [1]ferrocenophane, (1,1′-ferrocenediyl)dimethylsilane.[15] These polymers may have interesting optical, electronic, and magnetic behavior. The oligo(ferrocenyldimethyl-silanes) with the general formula $FcSiMe_2[(\eta^5-C_5H_4)-Fe(\eta^5-C_5H_4SiMe_2)]_nFc$ [$Fc = (\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)$, $n = 0-7$] can be prepared by the anionic ROP of (1,1′-ferrocenediyl)dimethylsilane.[16] The structure observed for the pentamer ($n = 3$) appears to be a good model for the corresponding prototypical high polymer.[16a,d] We have already investigated the interaction of β-CD with the dimer and trimer ($n = 0$ and 1, respectively).[17] In the present work, we describe the synthesis and solid-state characterization of γ-CD inclusion compounds containing the two oligomers. For comparison, the corresponding ferrocene inclusion compound has also been prepared and characterized.

Experimental Section

General Comments. All air-sensitive reactions and ma-nipulations were performed under nitrogen, using standard Schlenk techniques. Solvents were predried over sodium wire (*n*-hexane) or calcium hydride (dichloromethane) and distilled under argon from sodium-benzophenone (*n*-hexane) or calcium hydride (dichloromethane). γ-CD was kindly donated by Wacker-Chemie (Germany), and ferrocene (**1**) was obtained from Aldrich. Monolithioferrocene[18] and (1,1′-ferrocenediyl)-dimethylsilane[17a] were prepared according to literature pro-cedures. The dimer diferrocenyldimethylsilane (**2**) and the trimer 1,1′-bis(ferrocenyldimethylsilyl)ferrocene (**3**) were pre-pared by column chromatography on alumina of the oligomeric mixture obtained by the reaction of (1,1′-ferrocenediyl)dim-ethylsilane with monolithioferrocene.[16a,d,17,19]

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 X-ray diffraction (XRD) data were collected on a Philips X'pert diffractometer using Cu Kα radiation filtered by Ni ($\lambda = 1.5418$ Å). Thermogravimetric

analysis (TGA) was 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 Mod 7000 FTIR spectrophotometer using KBr pellets. 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 ^{1}H 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 ^{1}H 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 tetramethylsilane.

Synthesis of γ-CD–Ferrocene Inclusion Compound (1a). A solution of ferrocene (0.059 g, 0.3 mmol) in CH$_2$Cl$_2$ (0.4 mL) was added to a solution of γ-CD (0.40 g, 0.3 mmol) in water (1.0 mL) at 50 °C. A homogeneous solid product precipitated slowly at the water–dichloromethane interface. Stirring was stopped after 24 h, and the product was isolated by decantation, yield 120 mg (29.0%). Anal. Calcd for (C$_{48}$H$_{80}$O$_{40}$)·1.25(C$_{10}$H$_{10}$Fe)·12H$_2$O (1745.8): C, 41.62; H, 6.73; Fe, 4.00. Found: C, 41.73; H, 6.07; Fe, 3.99. TGA up to 100 °C revealed a sample weight loss of 11.8% (calcd for loss of 12H$_2$O, 12.4%). IR (KBr, cm^{-1}): ν 3403 vs, 2928 m, 2892 sh, 1639 m, 1413 m, 1384 sh, 1372 m, 1337 m, 1304 m, 1247 m, 1202 m, 1160 s, 1106 m, 1080 s, 1053 sh, 1028 vs, 1003 m, 938 m, 820 m, 760 m, 706 m, 610 sh, 581 m, 530 m, 494 m, 476 m. ^{13}C CP MAS NMR: δ 103.9 (γ-CD, C-1), 82.1 (γ-CD, C-4), 73.2, 72.0 (γ-CD, C-2,3,5), 68.2 (guest, Cp), 60.3 (γ-CD, C-6).

Synthesis of γ-CD–Diferrocenyldimethylsilane Inclu-sion Compound (2a). A solution of the dimer **2** (0.075 g, 0.18 mmol) in CH$_2$Cl$_2$ (0.6 mL) was added to a solution of γ-CD (0.46 g, 0.36 mmol) in water (1.0 mL) at 50 °C. The mixture was stirred under reflux for 4 days, during which time a homogeneous solid product formed at the water–dichlo-romethane interface. The product was isolated by decantation, yield 250 mg (46.7%). Anal. Calcd for 2(C$_{48}$H$_{80}$O$_{40}$)·(C$_{22}$H$_{24}$Fe$_2$-Si)·15H$_2$O (3292.7): C, 43.04; H, 6.55; Fe, 3.39. Found: C, 43.08; H 5.92; Fe, 3.44. TGA up to 100 °C revealed a sample weight loss of 6.7% (calcd for loss of 15H$_2$O, 8.2%). IR (KBr, cm^{-1}): ν 3384 vs, 2930 m, 2897 sh, 1639 m, 1416 m, 1383 sh, 1371 m, 1335 m, 1304 m, 1248 m, 1202 m, 1161 s, 1107 m, 1082 s, 1055 s, 1029 vs, 1004 m, 942 m, 823 m, 763 m, 707 m, 608 sh, 583 m, 529 m, 503 m, 450 m, 414 m. ^{13}C CP MAS NMR: δ 103.9 (γ-CD, C-1), 81.8 (γ-CD, C-4), 72.7 (γ-CD, C-2,3,5), 68.2 (guest, Cp), 60.3 (γ-CD, C-6), −1.2 (guest, SiMe$_2$). ^{29}Si CP MAS NMR: δ −6.4 ppm (guest, SiMe$_2$).

Synthesis of γ-CD–1,1′-Bis(ferrocenyldimethylsilyl)-ferrocene Inclusion Compound (3a). A solution of the trimer **3** (0.078 g, 0.12 mmol) in CH$_2$Cl$_2$ (1.0 mL) was added to a solution of γ-CD (0.45 g, 0.36 mmol) in water (1.5 mL) at 50 °C. The mixture was stirred under reflux for 4 days, during which time a homogeneous solid product formed at the water–dichloromethane interface. The product was isolated by de-cantation, yield 180 mg (33.8%). Anal. Calcd for 3(C$_{48}$H$_{80}$O$_{40}$)·(C$_{34}$H$_{38}$Fe$_3$Si$_2$)·40H$_2$O (5282.5): C, 40.47; H, 6.83; Fe, 3.17. Found: C, 40.25; H, 6.09; Fe, 2.93. TGA up to 100 °C revealed a sample weight loss of 13.0% (calcd for loss of 40H$_2$O, 13.6%). IR (KBr, cm^{-1}): ν 3416 vs, 2929 m, 2897 sh, 1642 m, 1419 m, 1384 m, 1372 m, 1340 m, 1304 m, 1249 m, 1200 m, 1161 s, 1107 m, 1080 s, 1055 s, 1029 vs, 1002 m, 941 m, 861 m, 820 m, 797 m, 762 m, 706 m, 609 sh, 582 m, 530 m, 483 m. ^{13}C CP MAS NMR: δ 103.9 (γ-CD, C-1), 82.3 (γ-CD, C-4), 73.5, 72.0 (γ-CD, C-2,3,5), 67.8 (guest, Cp), 60.3 (γ-CD, C-6), −1.1 (guest, SiMe$_2$). ^{29}Si CP MAS NMR: δ −6.4, −6.9 ppm (guest, SiMe$_2$).

Results and Discussion

Mixing of an aqueous solution of γ-CD with a solution of ferrocene (**1**), diferrocenyldimethylsilane (**2**), or 1,1′-bis(ferro-cenyldimethylsilyl)ferrocene (**3**) in dichloromethane resulted

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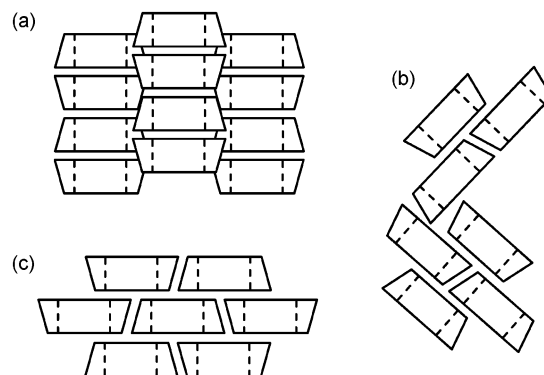
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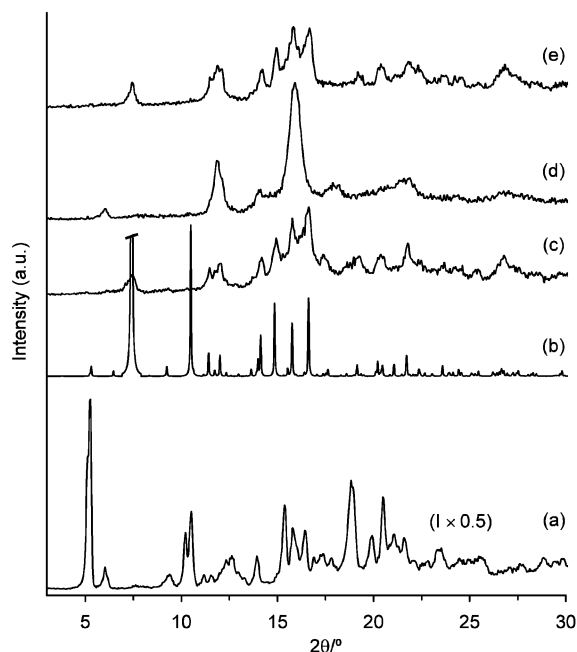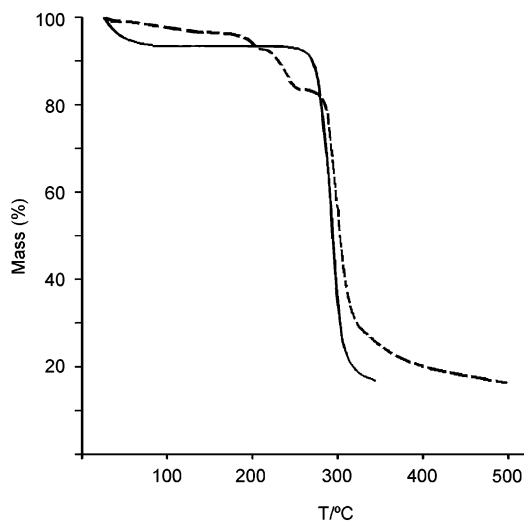
Figure 1. Experimental (a, c−e) and simulated (b) powder XRD patterns of (a) pristine γ-CD hydrate, (b) the 1:1 complex of γ-CD with 1-propanol, (c) the γ-CD−ferrocene inclusion compound (**1a**), (d) the γ-CD−diferrocenyldimethylsilane inclusion compound (**2a**), and (e) the γ-CD−1,1′-bis(ferrocenyldimethylsilyl)ferrocene inclusion compound (**3a**). The program PowderCell[21] was used to produce the calculated pattern (b) using the crystal structure data reported in the literature.[20]

Figure 2. Schematic representation of the most common packing structures for cyclodextrin complexes: (a) the head-to-head channel-type, (b) the cage-type, and (c) the layer-type.

Figure 3. Thermogravimetric analysis profiles of the 2:1 γ-CD−diferrocenyldimethylsilane inclusion compound (**2a**) (−) and a physical mixture of γ-CD and diferrocenyldimethylsilane (**2**) in a 2:1 molar ratio (- - -).

in the slow formation of pale yellow precipitates at the interface between the two solutions. Elemental analyses of the final isolated solids, designated as **1a**, **2a**, and **3a**, indicated host:guest molar ratios of 4:5, 2:1, and 3:1, respectively. The formulations for **2a** and **3a** show that the reactant stoichiometric ratios were maintained in the final isolated solids. The 4:5 ratio for **1a** deviates from the expected value of 1:1,[14a] although an identical inclusion ratio was recently reported in a single-crystal X-ray study of a β-CD−ferrocene inclusion compound.[14d] The products were further characterized in the solid state by powder XRD, TGA, and ^{13}C/^{29}Si MAS NMR spectroscopy.

Powder XRD. Figure 1 shows the powder XRD patterns measured for pristine γ-CD hydrate and compounds **1a**−**3a**. Also shown is a simulated powder diffraction pattern calculated using the crystal structure data for the 1:1 inclusion compound between γ-CD and 1-propanol.[20] The crystal structures of CD complexes are classified mainly into three types: channel-type, cage-type, and layer-type (Figure 2).[1,2] Pristine γ-CD hydrate adopts a cage-type structure, also referred to as a "herringbone" arrangement in which the cavity of each molecule is blocked by neighboring molecules. This structure converts to a channel structure in the presence of a suitable guest molecule. Thus, the γ-CD·1-propanol and γ-CD·methanol inclusion complexes crystallize with the tetragonal space group $P42_12$ and exhibit a columnar structure consisting of CD molecules stacked on top of each other along the crystallographic c-axis.[20,22] It is clear from Figure 1 that the reflec-

tions observed for compounds **1a** and **3a** match those calculated for the γ-CD·1-propanol inclusion complex, but are different from those for pristine γ-CD hydrate. This strongly supports the presence of channel-type structures in which ferrocene and 1,1′-bis(ferrocenyldimethylsilyl)ferrocene molecules are included within the cylindrical cavities of γ-CD. The powder diffraction pattern for compound **2a** is less well-defined. Although there are similarities between some of the gross features present in this pattern and those present in the patterns for **1a** and **3a**, there also some important differences. In particular, the lowest angle peak for **1a** and **3a** is at 7.5° 2θ, which is indexed as the (200) reflection and is a fingerprint for crystalline γ-CD inclusion complexes with channel-type structures.[9g] The first peak observed for **2a** is at 6.0° 2θ, and no peak is present at about 7.5° 2θ. Therefore, we cannot be certain about the type of crystal packing present in compound **2a**. However, the fact that the powder diffraction pattern is different from that for pristine γ-CD is a good indication for the formation of a true inclusion compound.[4]

Thermogravimetric Analysis. The γ-CD−diferrocenyldimethylsilane inclusion compound (**2a**) exhibits two steps in the TGA curve from room temperature up to 350 °C (Figure 3). Similar behavior was observed for compounds **1a** and **3a** (not

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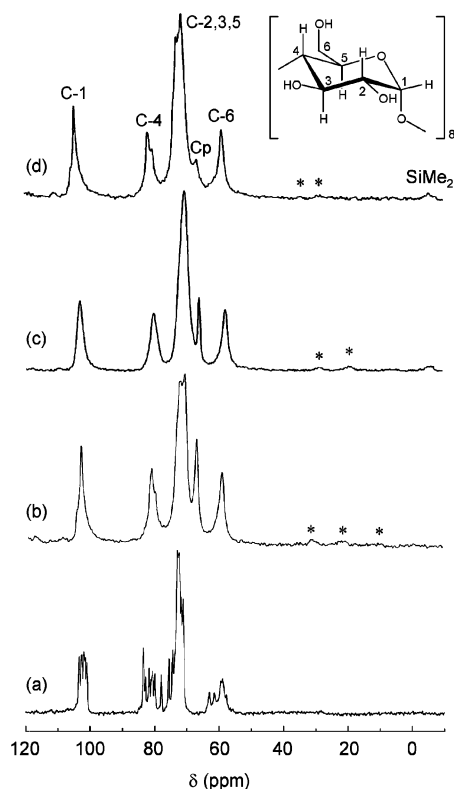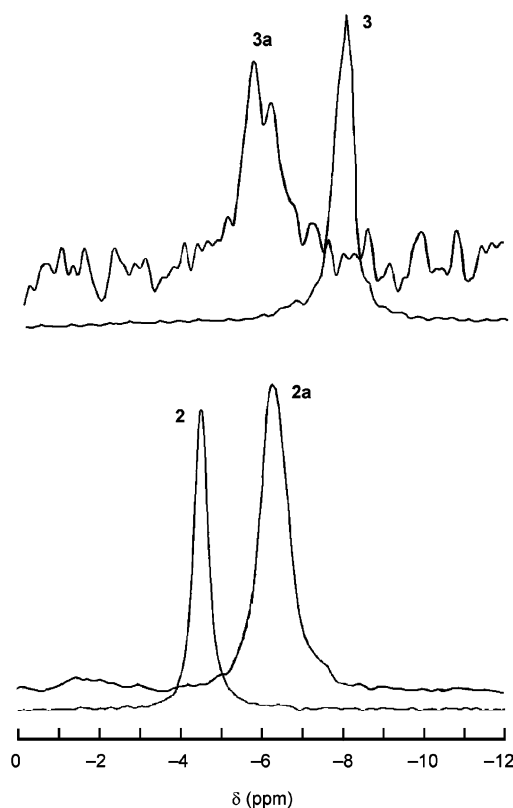
Figure 4. Solid-state ^{13}C CP MAS NMR spectra of (a) pristine γ-CD hydrate, (b) the γ-CD−ferrocene inclusion compound (**1a**), (c) the γ-CD−diferrocenyldimethylsilane inclusion compound (**2a**), and (d) the γ-CD−1,1′-bis(ferrocenyldimethylsilyl)ferrocene inclusion compound (**3a**). Spinning sidebands are denoted by asterisks.

shown). The first step, which takes place up to about 100 °C, is due to the removal of water molecules located in the γ-CD cavities and also in the interstices between the macrocycles. The observed mass losses for this step were consistent with elemental analyses and indicated that the number of water molecules per γ-CD molecule was about 12, 7, and 13 for **1a**, **2a**, and **3a**, respectively. The three inclusion compounds decompose abruptly around 300 °C in a single step. In contrast, TGA of a 2:1 physical mixture of γ-CD and diferrocenyldimethylsilane (**2**) reveals two separate mass losses (Figure 3), which correspond to the zones where compound **2** sublimes (175−250 °C) and γ-CD melts and decomposes (260−340 °C). The trace for **2a** therefore shows that the thermal behavior of the organometallic guest is modified by inclusion in γ-CD. In fact, the release of the guest and the decomposition of the host probably occur simultaneously in the temperature range 250−310 °C. Although similar results were obtained for the γ-CD−1,1′-bis(ferrocenyldimethylsilyl)ferrocene inclusion compound (**3a**) (that is, no mass loss in the temperature range 100−225 °C), we cannot conclude that the organometallic molecule gained thermal stability by inclusion in γ-CD because the sublimation/decomposition point for the pure trimer **3** is at least as high as the decomposition point for **3a**. For the γ-CD−ferrocene inclusion compound (**1a**), a gradual mass loss of about 3% takes place in the temperature range 80−225 °C, which could be due to the partial release of ferrocene (the total amount of ferrocene present in the initial complex is equivalent to 11.2 wt %).

Solid-State MAS NMR Spectroscopy. The ^{13}C CP MAS NMR spectra for pristine γ-CD and the inclusion compounds **1a−3a** are shown in Figure 4. The spectrum for the γ-CD−ferrocene inclusion compound (**1a**) is in agreement with that reported previously.[23] Like β-CD hydrate, γ-CD hydrate exhibits multiple resonances for each type of carbon atom,

Figure 5. Solid-state ^{29}Si CP MAS NMR spectra of diferrocenyldimethylsilane (**2**), 1,1′-bis(ferrocenyldimethylsilyl)ferrocene (**3**), and the corresponding γ-CD inclusion compounds **2a** and **3a**.

assigned to C-1 (100−105 ppm), C-4 (77−84 ppm), C-2,3,5 (71−76 ppm), and C-6 (58−64 ppm). This has been mainly correlated with different torsion angles about the (1→4) linkages for C-1 and C-4[24] and with torsion angles describing the orientation of the hydroxyl groups.[25] In contrast, the corresponding carbons for the inclusion compounds are observed mostly as single broad peaks with little or no structure. This is a common result for CD channel-type inclusion compounds containing either organic or organometallic guests, such as organic polymers[9,13] and half-sandwich molybdenum carbonyl complexes,[26] and can be attributed to an increase in the symmetry of the γ-CD macrocycle upon inclusion complexation. In other words, encapsulation of the guest molecule induces the ring to adopt a more symmetrical conformation, with each glucose unit in a similar environment. All of the spectra for the inclusion compounds contain a sharp peak at 68 ppm for the Cp carbon atoms of the guest molecules, unshifted compared with the corresponding signal for the free compounds **1−3**. The spectra for **2a** and **3a** also contain a weak broad peak around 0 ppm for the bridging dimethylsilyl groups.

^{29}Si CP MAS NMR spectra were also recorded for the pure oligo(ferrocenyldimethylsilanes) and the corresponding inclusion compounds (Figure 5). The dimer **2** and the trimer **3** exhibit single peaks at −5.3 and −8.0 ppm, respectively, for the bridging dimethylsilyl groups. These values are shifted by

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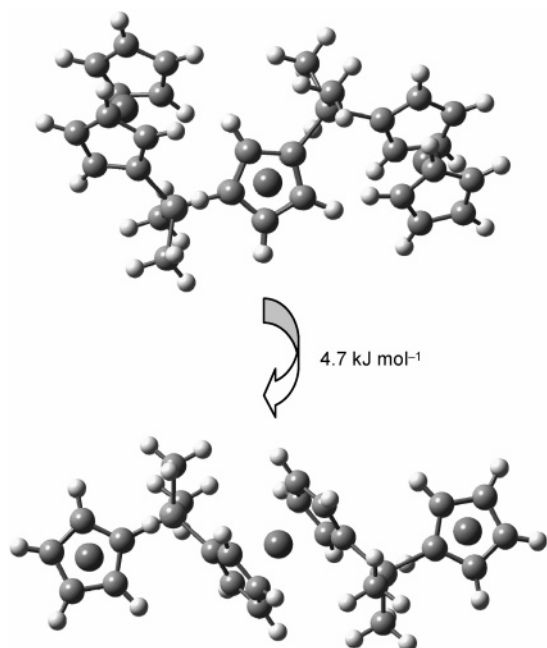
Figure 6. The lowest and second lowest energy conformations of the trimer **3**, as determined by ab initio calculations.[17b] The second lowest energy form mimics the extended structure found by X-ray crystallography.[16b,c]

Figure 7. Possible inclusion mode for the 3:1 γ-CD−1,1′-bis(ferrocenyldimethylsilyl)ferrocene inclusion compound (**3a**), obtained by adjusting the center of mass of the rigid host and guest blocks. All of the host···guest contacts in this structure are larger than 2.2 pm.

about 1.4 ppm compared with the solution spectra, which contain sharp resonances at -6.6 ± 0.1 ppm for the interior SiMe$_2$ groups. Interestingly, the resonances for these groups in the inclusion compounds have chemical shifts very close to those observed for compounds **2** and **3** in solution: -6.4 ppm for **2a** and $-6.4/-6.9$ ppm for **3a**. The presence of two resolved peaks for **3a** suggests that there are two slightly different environments for SiMe$_2$ groups of encapsulated guest molecules. The shift differences observed between the solid-state ^{29}Si NMR spectra for **2** and **2a** (and **3** and **3a**) are probably due to differences in the bulk susceptibility of the compounds. Hence, the fact that the resonances for the inclusion compounds are unshifted compared with the corresponding signals in the solution spectra of the free oligo(ferrocenyldimethylsilanes) is an additional proof that the organometallic molecules are isolated from each other in the cyclodextrin cavities as in solution.

Of particular interest in this work is the likely inclusion mode for compound **3a**. The presence of a channel-type structure with a 3:1 (host-to-guest) stoichiometry means that we have to consider the possibility of fitting one organometallic trimer within the cavities of three interacting γ-CD molecules. This arrangement was evaluated by a simple geometrical approach, building up a possible structure from the optimized molecular structure of the trimer **3** (Figure 6),[17b] and the crystal structure of the above-mentioned γ-CD·methanol inclusion complex with channel-type packing.[22] As shown in Figure 7, this simple model reveals that there is enough space to accommodate the trimer inside the γ-CD cavities and, furthermore, that the extended conformation of the guest allows a maximum interaction of each ferrocenyl moiety with each γ-CD cavity, keeping the CD skeleton of the crystalline structure unchanged.
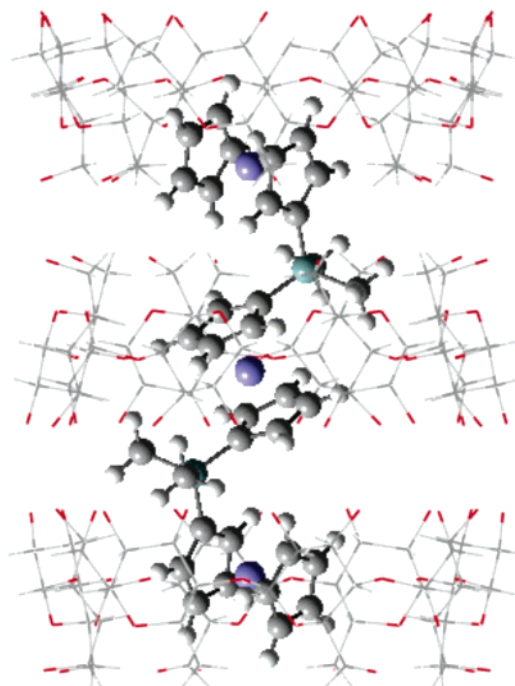
Concluding Remarks

This work has demonstrated that oligo(ferrocenyldimethylsilanes) form crystalline inclusion complexes with γ-cyclodextrin. Of particular interest is the fact that the trimer 1,1′-bis(ferrocenyldimethylsilyl)ferrocene forms a 3:1 complex with channel-type packing. This type of crystal packing is the one always found for inclusion complexes comprising organic polymers and also silicon-containing polymers such as poly(dimethylsiloxanes) and poly(dimethylsilanes). Simple geometrical considerations have indicated that the host−guest fit between the trimer and γ-CD is particularly favorable, allowing us to speculate that higher oligo(ferrocenylsilanes) and even poly(ferrocenylsilanes) should be able to form inclusion complexes with γ-CD, leading to a new family of organic−organometallic hybrids with potentially interesting optical, magnetic, or electrochemical properties.

OM050654M