

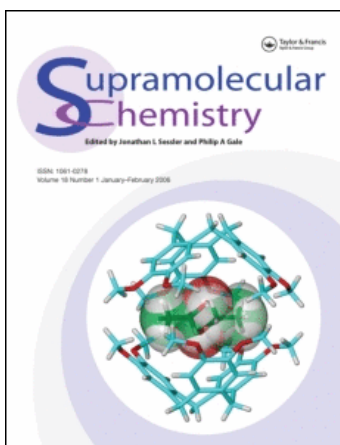
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### Solid State Confinement of Ferrocene by Calixarenes

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# Solid State Confinement of Ferrocene by Calixarenes

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**Combinations of ferrocene with unsubstituted calix[n]arenes,  $n = 4$  and 5, in toluene afford crystalline inclusion complexes (calix[4]arene)<sub>3</sub>(ferrocene) [hexagonal,  $a = 14.7797(4)$ ,  $c = 18.4400(4)$  Å,  $P6_3/m$ ,  $\rho = 1.389$  g.cm<sup>-3</sup>,  $Z = 2$ ,  $R_1 = 0.0963$  (on 1401 observed data [ $I > 2\sigma(I)$ ])] as a lattice-type inclusion complex, and (calix[5]arene)(toluene)<sub>0.55</sub>(ferrocene)<sub>0.45</sub> [monoclinic,  $a = 9.6908(8)$ ,  $b = 15.069(1)$ ,  $c = 22.957(1)$  Å,  $\beta = 90.155(5)^\circ$ ,  $P2_1/m$ ,  $\rho = 1.318$  g.cm<sup>-3</sup>,  $Z = 4$ ,  $R_1 = 0.1005$  (on 3130 observed data [ $I > 2\sigma(I)$ ])], that shows endo-cavity complexation of ferrocene by the calixarene.**

**Keywords:** Solid state confinement; Ferrocene; Calixarenes; Supramolecular complexation

## INTRODUCTION

Supramolecular complexation of organometallic compounds may be beneficial in that complexes often show altered properties with, for instance, intercalation compounds showing improved catalytic and physical properties [1,2]. The supramolecular chemistry of the archetypical organometallic complex, ferrocene [Fe(Cp)<sub>2</sub>] Cp=cyclopentadienyl, has been developing, although most studies to date have focused on the inclusion chemistry of ferrocene with cyclodextrins [3–7]. A 2:1 complex is formed between  $\alpha$ -cyclodextrin and ferrocene, while the larger  $\beta$ - and  $\gamma$ -cyclodextrins form 1:1 complexes. Inclusion complexes of [CpFe(arene)]<sup>+</sup> species are known with cyclodextrin host molecules [8–10] and the arene-based container molecule cyclotrimeratrylene [11,12]. Ferrocene has also been bound within an octamine based hemicarcerand [13], and a square

cyclophane [14,15]. Furthermore, some lattice-type inclusion complexes with ferrocene as a guest molecule have been reported [16–18]. Recently the entrapment of ferrocenes by a deep-cavity 4,4'-bipyridine: calixresorcin[4]arene hydrogen bonded complex was described by MacGillivray *et al.* [19]. Reported herein are the solid state complexes of ferrocene with calix[4]arene **1** or calix[5]arene **2**. The calixarenes are cyclic phenolic molecules that show a rich inclusion chemistry with a variety of host molecules [20]. Calix[4,5]arenes often adopt a cone conformation creating a molecular cavity that can complex even relatively large guest molecules. Calix[5]arenes, for instance, are known to form solid state host–guest complexes with large inorganic cage clusters such as o-carborane [21] and fullerene-C<sub>60</sub> [22,23].

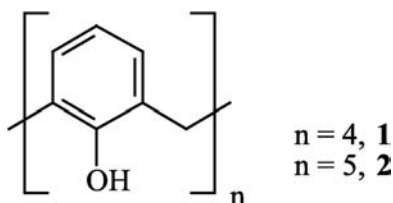
## EXPERIMENTAL SECTION

### Synthesis

(Calix[4]arene)<sub>3</sub>(ferrocene) **3**: Ferrocene (6.2 mg,  $3.2 \times 10^{-2}$  mmol) and calix[4]arene (17.0 mg,  $1.5 \times 10^{-2}$  mmol) were dissolved separately in toluene, mixed and allowed to stand. Yellow-orange crystals grew overnight. Found C 77.3, H 5.6, Fe 3.7; calc C 77.4, H 5.7, Fe 3.8 %.

(Calix[5]arene)(ferrocene)<sub>0.45</sub>(toluene)<sub>0.55</sub> **4**: Ferrocene (1.6 mg,  $8.7 \times 10^{-3}$  mmol) and calix[5]arene (4.2 mg,  $7.9 \times 10^{-3}$  mmol) were dissolved separately in toluene, mixed and allowed to stand. Yellow crystals grew after a few days on evaporation of all mother liquor. Meaningful microanalysis could not

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be obtained as crystals of **4** were contaminated with fine calix[5]arene needles.

### Structure Determinations

X-ray data were collected at 123(1) K on an Enraf-Nonius KappaCCD single crystal diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data were corrected for Lorentzian and polarisation effects but not absorption. The structures were solved by direct methods with SHELXS-97 and refined by full matrix least-squares on  $F^2$  using SHELXL-97. Details of the data collection and structure refinement are given in Table I, with additional information outlined below. Fractional atomic coordinates, anisotropic displacement parameters, bond lengths and angles and observed and calculated structure factors are available as supplementary data. For (calix[4]arene) $_3$ (ferrocene) **3**: All non-hydrogen atoms were refined anisotropically. C-H hydrogen atoms were fixed at geometrically estimated positions with a riding refinement. Ferrocene displayed a symmetry imposed disorder with the five Cp carbon positions disordered over six sites, hence each ferrocene C was refined with 83.33% occupancy. For (calix[5]arene)(ferrocene) $_{0.45}$ (toluene) $_{0.55}$  **4**: All non-hydrogen atoms aside from the toluene and ferrocene C atoms were refined anisotropically. C-H hydrogen atoms were fixed at geometrically estimated positions with a riding refinement. Occupancies of disordered guest molecules were estimated by an analysis of displacement parameters. A 50:50 ferrocene:toluene model was considered, however it led to unacceptably high  $U_{\text{iso}}$  values.

### RESULTS AND DISCUSSION

Evaporation of a mixture of **1** and ferrocene in toluene, in proportions ranging from 1:1 to a large excess of ferrocene, yields yellow-orange crystals of (calix[4]arene) $_3$ (ferrocene) **3**. The complex crystallises in a hexagonal cell and the structure was determined by X-ray diffraction techniques. Calix[4]arene molecules within the structure adopt a cone conformation but do not complex guest molecules in an *endo*-cavity fashion as expected on size and shape considerations (see below). Instead, the

TABLE I Crystal structure data and details of structure refinement for **3** and **4**

	<b>3</b>	<b>4</b>
Formula	C $_{94}$ H $_{82}$ FeO $_{12}$	C $_{43.35}$ H $_{38.9}$ Fe $_{0.45}$ O $_5$
$M_r$ (g mol $^{-1}$ )	1459.45	664.98
Crystal system	Trigonal (hexagonal)	Monoclinic
Space group	$P6_3/m$	$P2_1/m$
$a$ (Å)	14.7797(4)	9.6908(8)
$b$ (Å)	= $a$	15.069(1)
$c$ (Å)	18.4400(4)	22.957(1)
$\beta$ (°)		90.155(5)
$V$ (Å $^3$ )	3488.4(2)	3352.4(4)
$Z$	2	4
$\rho_{\text{calc}}$ (g cm $^{-3}$ )	1.389	1.318
Crystal description	Prismatic	Block
Colour	Yellow–orange	Yellow
Crystal size (mm)	0.35 $\times$ 0.25 $\times$ 0.13	0.35 $\times$ 0.15 $\times$ 0.10
$\mu$ (mm $^{-1}$ )	0.287	0.27
$\theta$ max (°)	27.07	27.50
Reflns collected	38705	24280
Unique reflns	2642	7225
$R_{\text{int}}$	0.092	0.144
Obs refln $I > 2\sigma(I)$	1401	3130
Parameters	174	515
$R_1$ (obs data)	0.0963	0.1005
$W r_2$ (all data)	0.2822	0.2537
$S$	1.031	1.032

calix[4]arenes associate into trimers. The trimer arrangement of calix[4]arenes has three-fold symmetry, with one phenyl face of each calixarene directed into the bowl of an adjacent calixarene such that it is virtually coplanar with one arene ring of this adjacent calixarene (angle between planes 3.8°) at ring centroid...centroid separation 4.04 Å. Guest ferrocene molecules, which are disordered due to the hexagonal symmetry of the crystals, are located in pockets created by packing of the calix[4]arene trimers (Fig. 1). The closest nonhydrogen contact

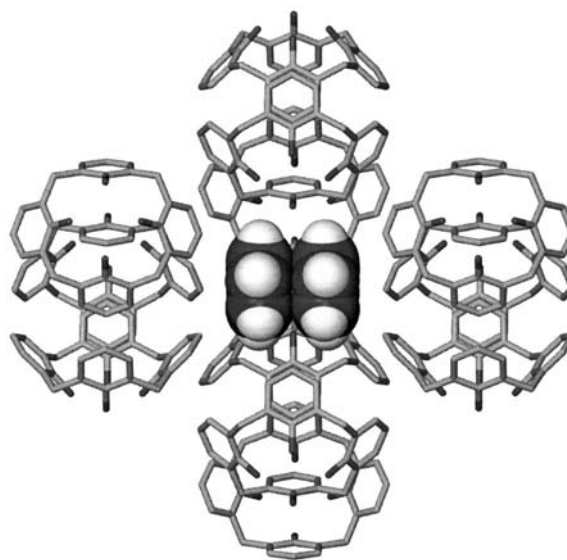


FIGURE 1 Section of the crystal structure of (calix[4]arene) $_3$ (ferrocene) **3** showing the entrapment of guest ferrocene by calix[4]arene trimers, calixarenes in front of the ferrocene are excluded for clarity.

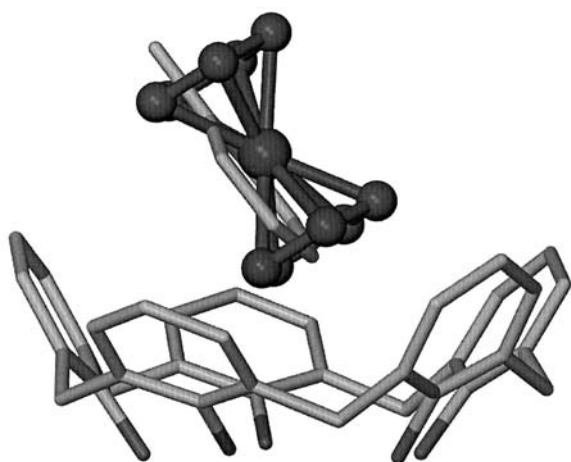


FIGURE 2 Host-guest species of  $(\text{calix}[5]\text{arene})(\text{ferrocene})_{0.45}(\text{toluene})_{0.55}$  **4**. The toluene and ferrocene guest molecules show a static disorder (see text).

between the ferrocene Cp rings and calixarene is 3.29 Å between a Cp C and calixarene phenolic O, the closest C...C distance is 3.45 Å. Previously reported examples of lattice-type inclusion complexes of ferrocene all have ferrocene guest molecules within channels created by the packing motif of the co-crystallising molecule [16–18]. Complex **3**, on the other hand, shows a complete entrapment of ferrocene by the calix[4]arene packing.

This structure is typical of the inclusion complexes of calix[4]arene, and structurally similar 3:1 crystalline host-guest complexes of calix[4]arene with guest acetonitrile, water, chloroform or acetone have been reported, all with similar unit cell parameters [24–26]. A 1:1 complex with acetone, where the acetone is bound within the calix[4]arene, is also known [26], however the cavity of calix[4]arene is too small to allow for the *endo*-cavity complexation of ferrocene in an analogous manner. The cavity size of related calixresorcin[4]arenes has been extended, either through the covalent formation of a hemi-carcerand or through attaching bipyridine arms through hydrogen bonds, to allow for the complexation of metallocenes [13,19], however simply using a larger calixarene also results in the *endo*-cavity complexation of ferrocene in the solid state as is described below.

Slow evaporation of a roughly equimolar mixture of **2** and ferrocene in toluene yields yellow crystals of  $(\text{calix}[5]\text{arene})(\text{ferrocene})_{0.45}(\text{toluene})_{0.55}$  **4**. A similar reaction in  $\text{CH}_3\text{CN}$  does not result in the inclusion of ferrocene, instead giving the crystalline acetonitrile clathrate  $(\text{calix}[5]\text{arene})(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})$ ,<sup>†</sup> that is very similar to the previously reported acetone clathrate [27]. The structure of complex **4** was determined by single crystal X-ray diffraction techniques; the complex crystallises in a monoclinic

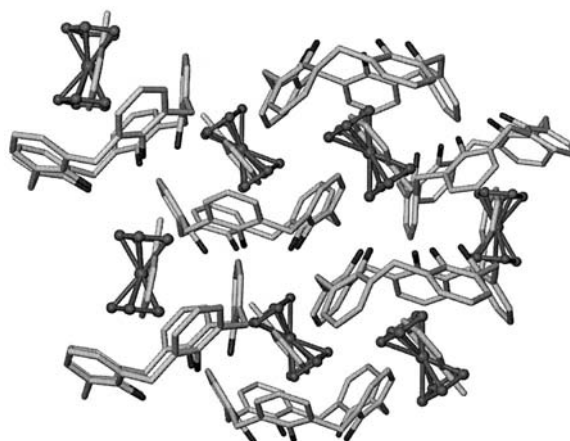


FIGURE 3 Packing diagram for  $(\text{calix}[5]\text{arene})(\text{ferrocene})_{0.45}(\text{toluene})_{0.55}$  **4**.

cell and features *endo*-cavity complexation of both ferrocene and toluene guest molecules. Complex **4** is an example of second sphere coordination of a transition metal by a calixarene, of which there are few previous examples [19,28].

The host-guest species of **4** is shown in Fig. 2. Toluene and ferrocene guest molecules show a static disorder with both guests occupying approximately the same position within the calix[5]arene cavity. There are two crystallographically distinct host-guest species, both of which reside on centres of symmetry. The major difference between the two is the occupancy of the guest molecules; in one the toluene and ferrocene each have 50% occupancy, in the other the toluene:ferrocene occupancy is 60:40. There is no evidence that the occupancy of ferrocene relative to toluene is affected by increasing the concentration of the ferrocene, which is consistent with co-operative effects between supermolecules with ferrocene or toluene in the cavity. The toluene guest molecules are oriented such that they are nearly coplanar with one arene ring of their host calix[5]arene (angles between planes 9.1 and 8.4°) at ring centroid...centroid separations 3.97 and 3.98 Å, slightly long for typical  $\pi$ - $\pi$  interactions. The toluene methyl groups point out of the calixarene cavities. Not only are the ferrocene guest molecules included in similar positions to the toluene guest molecules within the calix[5]arene bowl but also they have an identical orientation; in both cases the toluene ring is coplanar with the ferrocene axis (defined as Cp centroid-Fe-Cp centroid). Interestingly, this orientation of the ferrocene does not allow for additional intermolecular interactions within the host-guest moiety such as  $\pi$  stacking or C-H... $\pi$  non-classical hydrogen bonds that were a feature of the 4,4'-bipyridine: calixresorcin[4]arene host-guest complex with ferrocene [19]. Packing of

<sup>†</sup>Unit cell parameters for  $(\text{calix}[5]\text{arene})(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})$  at 123(1) K: orthorhombic *P*,  $a = 9.4830(2)$ ,  $b = 15.1950(4)$ ,  $c = 22.5437(5)$  Å.

the host-guest complexes within the crystal lattice is similar to that of the previously reported acetone clathrate [27], and is shown in Fig. 3.

Surprisingly, in both complexes **3** and **4** the inclusion behaviour exhibited by the calixarene is similar to that already established with small organic guest molecules, although the solution state inclusion chemistry is not currently known. That ferrocene can be included in the same fashion augers well for continued study of the complexation of organometallic complexes by calixarenes in general, and it is notable in this context that the complexation of highly functionalised ferrocene derivatives by water soluble, anionic sulfonated calixarenes in aqueous media has also been reported [29,30].

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