Redox-active Cavitand Host Molecules containing Multiple Redox Centres, Syntheses and X-ray Crystal Structure of a Dichloromethane Inclusion Complex

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The synthesis and electrochemistry of two novel redox-active rigid cavitand hydrophobic host molecules **(4)** and **(7)**, both containing four ferrocene moieties, are reported; the single crystal X-ray structure of **(4)** reveals a dichloromethane guest molecule within the cavitand host cavity.

Cavitands are synthetic organic host molecules that contain rigid cavities of dimensions large enough to include simple organic and inorganic guest species.[1,2] The incorporation of redox-active centres into these preorganised[3] hydrophobic host compounds will lead to prototypes of new molecular sensory devices[4] capable of electrochemically recognising the inclusion of a guest in the cavitand cavity. Such compounds may also serve as a new class of redox catalyst, promoting redox reactions on an included guest substrate.

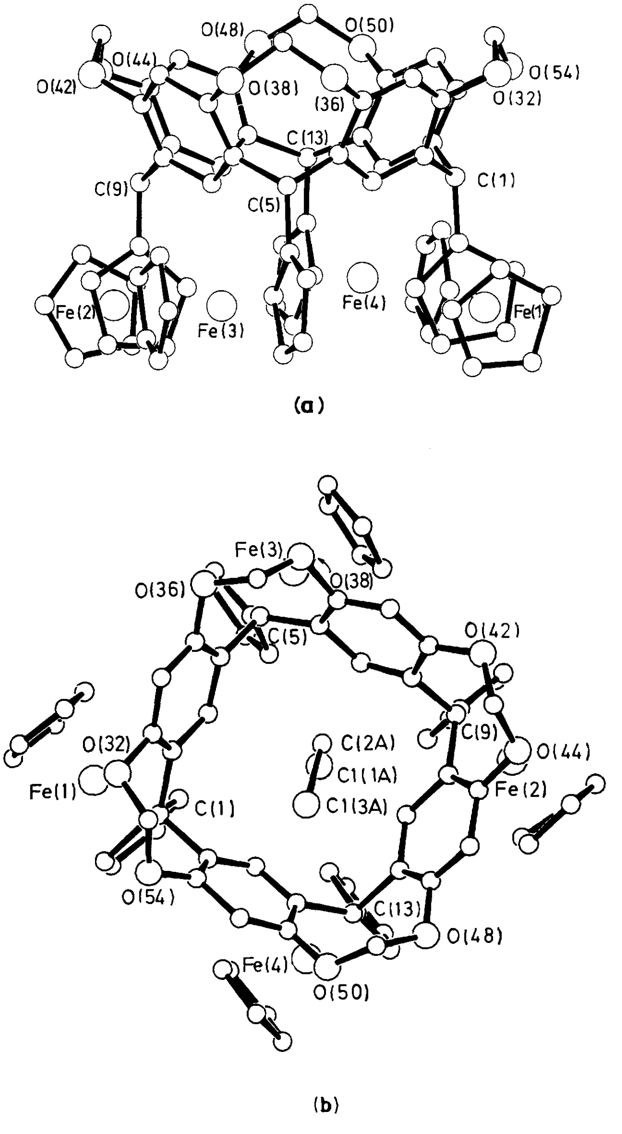

Figure 1. The crystal structure of **(4)** showing (a) the regular cone shape and (b) the inclusion of a dichloromethane guest molecule.

We report the preparation and electrochemical properties of two novel redox-active cavitand host molecules **(4)** and **(7)**, each containing four ferrocenyl moieties, and the single-crystal X-ray structure of **(4)** revealing the inclusion of a dichloromethane guest. The reaction of ferrocenecarbaldehyde **(1)** and resorcinol **(2)** in the presence of hydrochloric acid and ethanol gave the phenolic macrocycle **(3)**.[5] Subsequent reaction of **(3)** with $BrCH_2Cl$ in dry DMF (dimethylformamide) and K_2CO_3 gave a crude product which was purified by column chromatography (alumina, CH_2Cl_2) to give **(4)** as orange crystals (1% overall yield for two steps; not optimised). Condensing **(5)**[6] with an excess of 1,1′-bis-chlorocarbonylferrocene **(6)**[7] in the presence of triethylamine gave, after column chromatography (alumina, CH_2Cl_2), **(7)** as an orange crystalline solid (4% overall yield) with the ferrocene moieties lining the wall of the cavitand cavity. Elemental analyses, mass spectrometry, and ^1H and ^{13}C n.m.r. spectroscopy confirmed the proposed structures. Crystals of **(4)** suitable for X-ray structural investigation were obtained from dichloromethane–diethyl ether.† The structure consists of discrete molecules of **(4)** [shown in Figures 1(a) and (b)] together with four molecules of dichloromethane. The cavitand has a regular cone-shape in that the eight oxygens form an approximate plane [deviations O(32) −0.09, O(36) 0.12, O(38) 0.07, O(42) −0.05, O(44) −0.16, O(48) 0.17, O(50) 0.06, O(54) −0.11 Å] as do the four carbon atoms C(1), C(5), C(9), C(13) (deviations −0.09, 0.09, −0.09, 0.09 Å respectively). These two planes are approximately parallel (angle of intersection 1.0°). The four benzene rings are all tilted at similar angles from these two planes making angles of intersection between 58 and 62°.

One of the solvent molecules has full occupancy and this occupies a position within the cavity of the cavitand. Indeed, the position of Cl (1A) is only 0.2 Å from the centroid of the eight oxygen atoms [Figure 1(b)]. The other dichloromethane molecules which have only 50% occupancy are situated between the host molecules rather than within the cavity.

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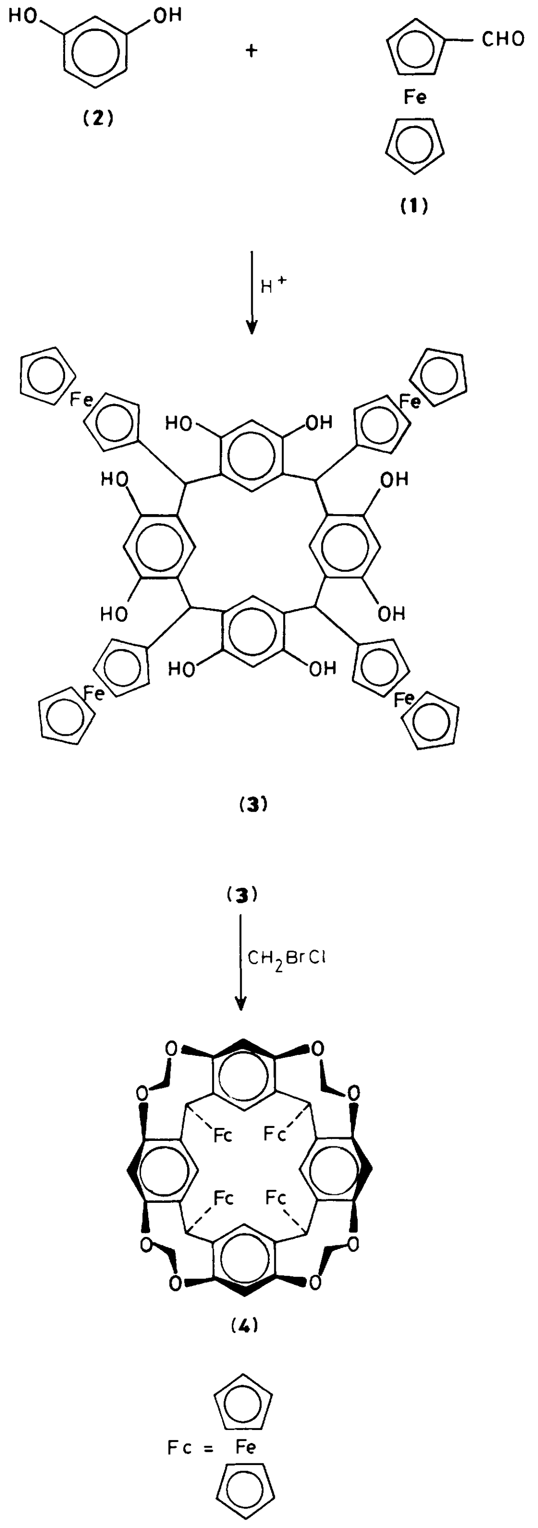
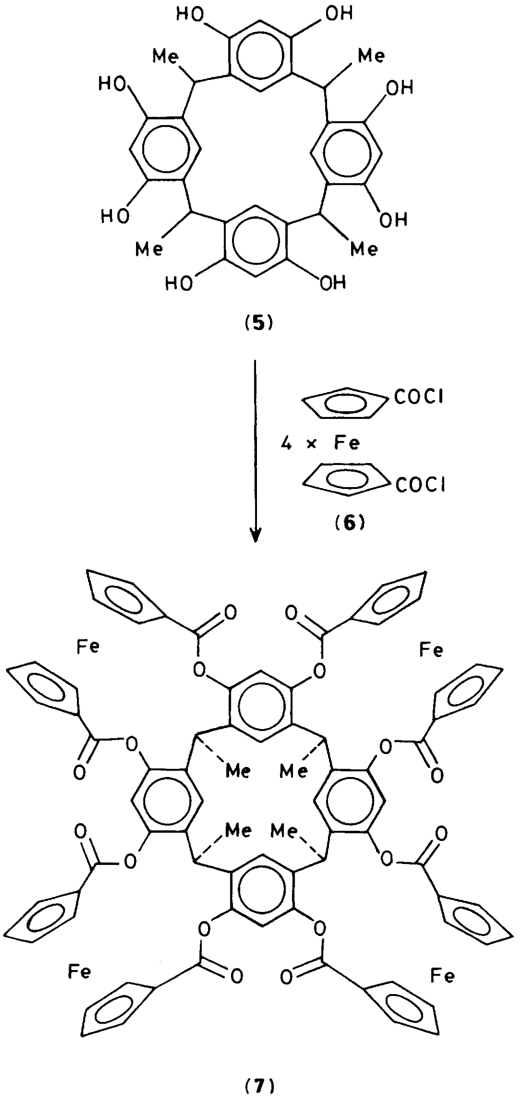
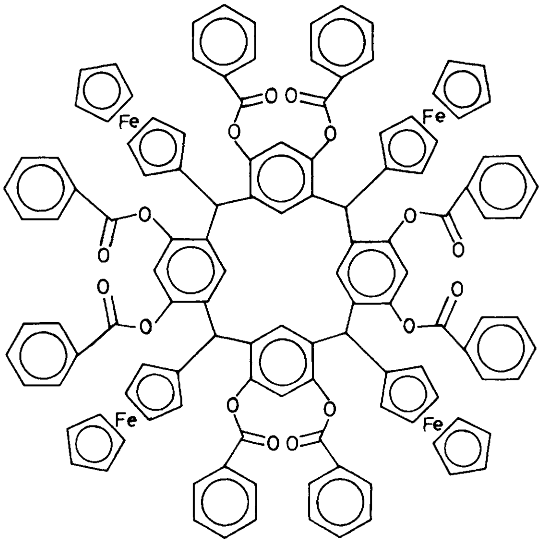
† *Crystal data*: **(4)**, $[Fe_4C_{76}O_8H_{56}].2.5CH_2Cl_2$, M = 2936.2, monoclinic, space group $P2_1/n$ a = 19.366(23), b = 12.812(11), c = 28.280(25) Å; β = 108.7(1)°, U = 6645.6 Å^3, $F(000)$ = 3012, D_m = 1.51 g cm^{-3}, D_c = 1.47 g cm^{-3}, Z = 4, Mo-K_α radiation (λ = 0.7107 Å), μ(Mo-K_α) = 11.3 cm^{-1}. 3873 independent reflections above background [$I > 2\sigma(I)$] were measured on a diffractometer. The structure was determined by heavy atom methods (the molecule together with solvent dichloromethane; one at full occupancy and three at half-occupancy with common C–Cl and Cl · · · Cl distances), and refined by full-matrix least-squares [Fe, anisotropic, C, O, Cl, H (in fixed positions) isotropic, to R 0.095 (R_w 0.097)]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.







(8)

The respective reversible cyclic voltammograms of (**4**) and (**7**) in dichloromethane gave an oxidation wave at +0.63 V and a reduction wave at +0.56 V (*vs.* standard calomel electrode, S.C.E.) for (**4**) and an oxidation wave at +1.14 V, a reduction wave at +1.07 V (S.C.E.) for (**7**). Coulometry showed both redox reactions to be four electron processes. This result suggests that all four respective ferrocene moieties present in (**4**) and (**7**) become oxidised in one step which is in contrast to the related macrocycle (**8**) exhibiting two, two electron reversible oxidation waves.[5]

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