X-Ray Structure of the α-Cyclodextrin–Ferrocene (2:1) Inclusion Compound

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The crystal structure of the α-cyclodextrin–ferrocene (2:1) inclusion compound has been determined by an X-ray analysis which shows that the ferrocene molecule with approximate D_{5d} symmetry is encapsulated by the dimer of the α-cyclodextrins in a tail-to-tail orientation and inclined by 42° relative to the six-fold axes of the α-cyclodextrins of the dimer.

Cyclodextrins (CDs) are cyclic oligosaccharides composed of six, seven, or eight α-1,4 linked D-glucose units and have hydrophobic cavities which enable them to form stable inclusion compounds with various compounds, ranging from organic molecules to small ions.[1,2] Extensive X-ray work on α-, β-, and γ-CD inclusion compounds has been carried out since they mimic biological macromolecules. Recently, CDs have received attention as second sphere ligands for transition metal complexes,[3] but only a few X-ray analyses on CD inclusion compounds of organometallic complexes[4] and metallo-organic complexes[5,6] have been reported. The CD inclusion compounds with ferrocene and its derivatives have been the most common CD adducts with organometallic complexes,[7,8] and structural studies on them by c.d.,[8] Mössbauer,[9] and NMR[10] spectroscopy and molecular mechanics calculations[11,12] on ferrocene complexation with CDs have been carried out. Here we report the first X-ray structure of an inclusion compound composed of CDs and ferrocene or ferrocene derivatives, α-CD–ferrocene (2:1), which gives a clear location of a guest molecule in an α-CD.

The two α-CDs with approximate six-fold axes form a dimer in a tail-to-tail orientation by extensive hydrogen bonding between the O(2) and O(3) secondary hydroxy groups; this completely encapsulates a ferrocene molecule in the hydrophobic cavity composed of the two α-CDs as shown in Figures 1 and 2.[13] These dimers are further connected by hydrogen bonding between the primary hydroxy groups and the water present as the medium, to form a one-dimensional channel along the c-axis. In the hydrophobic cavity of the dimer, iron and carbon atoms of the ferrocene are distinctly located by difference Fourier synthesis, showing that the ferrocene molecule is not disordered, although the hindered rotation around the five-fold axis of the ferrocene molecule seems to be still possible. The ferrocene molecule in the cavity is inclined by 42° from an axial orientation.

The two α-CD macrocycles of the dimer are almost parallel; the angle between the O(4) ether atoms planes is 2.3°. This tail-to-tail arranged dimer has a local two-fold axis which goes through iron atom (Figure 1). The interplanar distance between the O(4) atom planes of the α-CDs of the dimer is 6.7 Å, and the van der Waals diameter of the cavity is *ca.* 5.5 Å at the O(4) atoms and *ca.* 8.2 Å at the O(2) and O(3) secondary hydroxy groups near the bulge of the cavity, while the ferrocene molecule has a cyclindrical shape (6.7 Å height and 6.4 Å diameter). The size of the cavity shows that an axial or an equatorial orientation of the guest is unfavourable since the guest is loosely fitted into the cavity around the bulge and too tightly around the O(4) atoms. Interestingly, the macrocycles of the dimer are shifted laterally by *ca.* 1.3 Å to each other, indicating that the cavity of the dimer does not have a six-fold symmetry (Figures 1
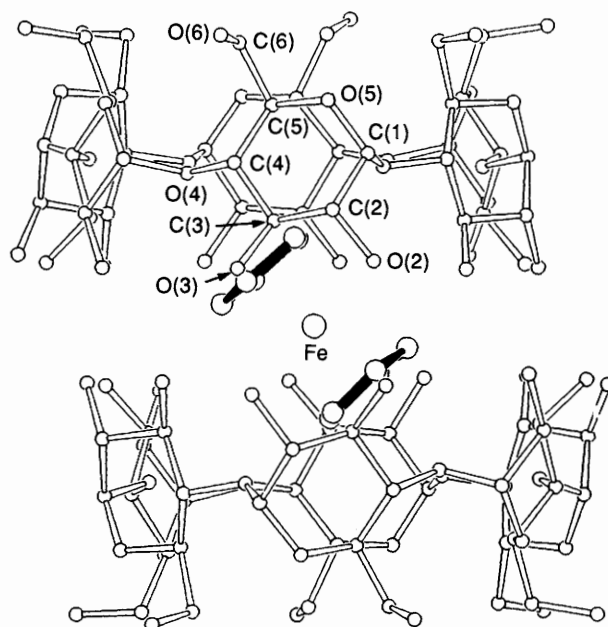
Figure 1. View of the α-cyclodextrin–ferrocene (2:1) inclusion compound along a local two-fold axis which goes through the Fe atom. Two macrocycles are shifted laterally by *ca.* 1.3 Å to each other. Water molecules are not drawn for the sake of clarity.

and 2). This shift plays an important role in fixing the ferrocene molecule in the cavity. The ferrocene molecule in the cavity follows this lateral shift of the macrocycles and all the carbon atoms of the cyclopentadienyl ring are in close contact to the α-CD macrocycles. Therefore, the ferrocene molecule is held in the cavity with the maximum amount of van der Waals stabilization. The overall structure of this α-CD–ferrocene (2:1) in the solid looks similar to that optimized in the gas phase by a molecular mechanics calculation.[11]

The ferrocene molecule in the cavity has an approximate D_{5d} symmetry, the cyclopentadienyl rings being mutually rotated by *ca.* 30° from the eclipsed orientation, which is in contrast with the nearly, or exactly, eclipsed ones found in crystalline or gaseous ferrocene.[13,14] Preference for the staggered conformation may be due to the two-fold symmetry of the hydrophobic cavity and the low rotational energy barrier (3.8 kJ mol⁻¹)[15] around the five-fold axis.

Experimental

α-CD–ferrocene (2:1) inclusion compound was prepared as

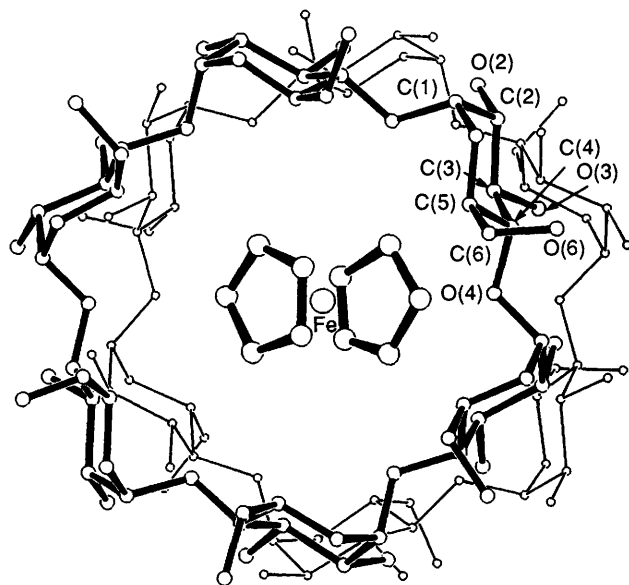**Figure 2.** View of the α-cyclodextrin–ferrocene (2:1) perpendicular to the O(4) ether atoms planes of the macrocycles. The bonds of the lower macrocycle are indicated by thin lines.

described in the previous paper.[8] Ferrocene-like orange-yellow crystals suitable for an X-ray experiment were obtained from slow cooling (80 to 40 °C) of an aqueous solution using a thermostat equipped with a temperature programmer. The crystal (0.62 × 0.30 × 0.35 mm) was sealed in a glass capillary with a drop of mother liquor to avoid crystal degradation and used for X-ray measurements on a Rigaku AFC-6A diffractometer.

Crystal Data for $2(C_6H_{10}O_5)_6 \cdot C_{10}H_{10}Fe \cdot 9H_2O$.—Triclinic, space group $P1$, $a = 13.864(5)$, $b = 13.900(6)$, $c = 15.694(9)$ Å, $\alpha = 94.34(7)$, $\beta = 87.78(6)$, $\gamma = 120.22(3)°$, $Z = 1$, $D_c = 1.46$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 2.52$ cm^{-1}. 7 039 Independent reflections [5 288 with $I > 3\sigma(I)$] were collected up to 55° in 2θ, using Mo-K_α radiation and a ω-scan mode at room temperature. The structure was solved with the aid of the structure of $(\alpha\text{-CD})_2 \cdot LiI_3 \cdot I_2 \cdot 8H_2O$[16] which is isomorphous with α-CD–ferrocene (2:1). The structure was refined to $R = 0.075$ and $R_w = 0.086$ by a block-diagonal least squares method,[17] using anisotropic temperature factors for all atoms. Atomic co-ordinates and thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallo-

graphic Data Centre; see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1990, Issue 1.

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