Molecular Encapsulation of Transition Metal Complexes in Cyclodextrins. Part 2. Synthesis and Crystal Structures of 2:1 Adducts between α-Cyclodextrin and Metallocenium Hexafluorophosphates [(η⁵-C₅H₅)₂M]PF₆(M=Fe, Co, Rh).

BERND KLINGERT* and GRETY RIHS
Central Research Laboratories, Ciba-Geigy Ltd., CH-4002 Basle, Switzerland

Abstract. The title metallocenium salts form crystalline 2:1 host:guest inclusion compounds with α-cyclodextrin, $[(\eta^5\text{-}C_5H_5)M]PF_6 \cdot 2\alpha\text{-CD} \cdot 8H_2O$ (1, M = Fe; 2, M = Co; 3, M = Rh). The X-ray crystal structures of 1 and 3, and the lattice constants, crystal system and space group of 2 have been determined. Crystal data: triclinic, space group $P1$ (No. 1), $Z = 1$; 1, $a = 13.865$ (2) Å, $b = 13.839$ (2) Å, $c = 15.520$ (2) Å, $\alpha = 91.43$ (2)°, $\beta = 85.81$ (2)°, $\gamma = 120.22$ (2)°, and $R_F = 0.089$ for 4257 observed MoK$_\alpha$ reflections $[I > 3\sigma(I)]$; 2, $a = 13.810$ (2) Å, $b = 13.872$ (2) Å, $c = 15.560$ (2) Å, $\alpha = 93.99$ (2)°, $\beta = 87.06$ (2)°, $\gamma = 120.04$ (2)°; 3, $a = 13.756$ (1) Å, $b = 13.863$ (1) Å, $c = 15.561$ (2) Å, $\alpha = 94.39$ (1)°, $\beta = 86.92$ (1)°, $\gamma = 119.89$ (1)°, and $R_F = 0.061$ for 11142 observed MoK$_\alpha$ reflections $[I > 3\sigma(I)]$. In the crystals of 1 and 3, two α-cyclodextrin molecules are arranged head-to-head to form a dimer by means of intermolecular hydrogen bonding across the secondary hydroxyl faces of adjacent α-CD monomers. The dimers are stacked along the crystallographic c axis to form a channel-type structure. The metallocenium cation is encapsulated within the cavity of the dimer, while the PF_6^- anion is located outside the cavity, being centered between the primary hydroxyl faces of adjacent dimers. Eight water molecules of hydration per asymmetric unit reside in the spaces between the α-CD columns. In view of the almost identical crystal data for 2 a similar structure can be assumed for the cobaltocenium adduct.

Key words. Cyclodextrin inclusion compound, metallocene, crystal structure.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82104 (76 pages).

1. Introduction

In the field of supramolecular chemistry the inclusion of transition metal complexes by a range of different host molecules has attracted considerable attention. Macrocyclic crown ethers, for example, have been shown to act as second-sphere ligands mainly for transition metal ammine complexes [1], while cyclodextrins (CDs) appear to be particularly suitable receptors for complexes bearing hydrophobic first-sphere ligands [2]. Most of the work concerning inclusion compounds of organometallic complexes with cyclodextrins has concentrated on ferrocene and its derivatives. Crystalline α-, β- and γ-CD adducts of ferrocenes have been isolated and characterized in the solid state by Harada and Takahashi [3], and on the basis of CPK molecular models, an axial inclusion geometry has been proposed for the 2:1 α-CD: ferrocene compound. Recent docking calculations of ferrocene complexation with

*Author for correspondence.

cyclodextrins reported by Menger and Sherrod [4] revealed a tilt of the ferrocene molecule against the α-CD axes of 40–45° in both the 1:1 and the 2:1 adduct.

However, unequivocal structural information regarding the inclusion geometry of ferrocene in cyclodextrins has not been obtained yet [5]. The only example of a crystallographically characterized adduct between a transition metal sandwich complex and cyclodextrins reported to date is [CpFe(Benzene)]$PF_6 \cdot 2\alpha$-CD $\cdot 8H_2O$ (Cp = η^5-C_5H_5) obtained recently in our laboratory and reported in Part 1 of this series [6]. Since the guest molecule of this adduct is structurally very closely related to metallocenium salts of the general formula [Cp_2M]PF_6, we carried out a systematic study on the adduct formation between these sandwich complexes and α-cyclodextrin.

2. Experimental

2.1. STARTING MATERIALS

α-Cyclodextrin was obtained from Fluka Chemie AG, [Cp_2Co]PF_6 from Aldrich, and used as received. The metallocenium hexafluorophosphates [Cp_2M]PF_6, M = Fe [7] and M = Rh [8] were prepared according to literature procedures.

2.2. PREPARATION OF THE INCLUSION COMPOUNDS

(**1**): 331 mg (1.0 mmol) [Cp_2Fe]PF_6 was dissolved in 30 mL of water at 80°C and a hot aqueous solution (20 mL) of 2.14 g (2.2 mmol) α-CD added. The hot solution was filtered and allowed to cool slowly to room temperature overnight during which time dark blue crystals of **1** were formed. The mother liquor was decanted, the crystals washed successively with water, ethanol and ether and dried *in vacuo*. Yield: 1.63 g (72%). Anal. Calcd. for $C_{82}H_{130}F_6FeO_{60}P \cdot 8H_2O$: C, 40.68; H, 6.08; F, 4.71; Fe, 2.31; P, 1.28. Found: C, 40.56; H, 6.17; F, 4.66; Fe, 2.30; P, 1.25.

The α-CD adducts **2** and **3** were prepared and isolated in essentially the same manner.

(**2**): yellow crystals, yield: 78%. Anal. Calcd. for $C_{82}H_{130}CoF_6O_{60}P \cdot 8H_2O$: C, 40.38; H, 6.86; Co, 2.21; F, 4.67; P, 1.27. Found: C, 40.50; H, 6.16; Co, 2.37; F, 4.66; P, 1.26.

(**3**): colourless crystals, yield: 91%. Anal. Calcd. for $C_{82}H_{130}F_6O_{60}PRh \cdot 8H_2O$: C, 39.91; H, 5.96; F, 4.62; P, 1.26; Rh, 4.17. Found: C, 40.42; H, 5.92; F, 4.71; P, 1.20; Rh, 4.20.

2.3. X-RAY STRUCTURAL ANALYSIS

The sample crystals were sealed with epoxy to the end of a glass fiber and showed no significant intensity decay during data collection. Intensity measurements were carried out on a Philips PW-1100 diffractometer (graphite monochromator, MoK_α radiation, $\theta/2\theta$ scan). The positions of the atoms of one CD molecule were taken from [6] and submitted to the subprogram ORIENT of the program system DIRDIF [9]. In subsequent difference Fourier maps all nonhydrogen atoms could be located. In **3** all nonhydrogen atoms and in **1** the heavier atoms Fe and P were

Table I. Crystal data for inclusion complexes 1–3

Compound	1	2	3
Formula	$[(C_5H_5)_2Fe]PF_6$ $\cdot 2(C_{36}H_{60}O_{30})$ $\cdot 8H_2O$	$[(C_5H_5)_2Co]PF_6$ $\cdot 2(C_{36}H_{60}O_{30})$ $\cdot 8H_2O$	$[(C_5H_5)_2Rh]PF_6$ $\cdot 2(C_{36}H_{60}O_{30})$ $\cdot 8H_2O$
lattice type	triclinic	triclinic	triclinic
space group	$P1$	$P1$	$P1$
T(K)	190	190	185
cell dimensions:			
a(Å)	13.865(2)	13.810(2)	13.756(1)
b(Å)	13.839(2)	13.872(2)	13.863(1)
c(Å)	15.520(1)	15.560(2)	15.561(2)
α(°)	91.43(2)	93.99(2)	94.39(1)
β(°)	85.81(2)	87.06(2)	86.92(1)
γ(°)	120.22(2)	120.04(2)	119.89(1)
V(Å^3)	2566	2573	2564
Z	1	1	1
$D_{calc} \times 10^{-3}$ (kg m^{-3})	1.566		1.598
θ-range (°)	3-25		3-29
No. of reflections	9459		14173
No. of reflections with $I > 3\sigma(I)$	4257		11142
Final No. of variables	673		1423
Final R	0.089		0.061

introduced with anisotropic thermal parameters into the least squares refinements. Because of the fewer number of observed reflections and of the twinned character of the crystal investigated of 1 the C and O atoms of 1 were refined isotropically. Crystallographic data of 1–3 are summarized in Table I. Final atomic coordinates of 3 are listed in Table II. In 1 the C-atoms of the Cp rings showed rather large temperature factors as a consequence of a disorder of the guest molecule.

3. Results and Discussion

Host-guest binding in solution to α-CD has been demonstrated for the ferrocenium cation by measurements of induced circular dichroism. A dimethylsulfoxide solution of $[Cp_2Fe]PF_6$ containing an excess of α-CD shows a negative induced Cotton effect at 450 nm, which is in agreement with the corresponding spectra of ferrocene [10] and [CpFe(Benzene)]PF$_6$ [6], respectively. In contrast, a positive ICD signal has been reported for an ethylene glycol solution of the ferrocenium salt containing β-cyclodextrin [10].

Co-crystallization of the title metallocenium salts and α-CD from aqueous solution afforded crystals of 1–3 suitable for X-ray crystallographic analysis. They were found to be isomorphous to those of the 2:1 α-CD adduct of [CpFe(Benzene)]PF$_6$ [6].

In the crystals of 1 and 3 two α-cyclodextrin molecules which have the characteristic bucket-shaped conformation are arranged head-to-head to form a dimer by

Table II. Fractional atomic coordinates of 3

Atom	x	y	z	Atom	x	y	z
				Guest molecules and Water molecules:			
RH1	0.016	−0.023	0.220	F2	−0.063(2)	−0.104(2)	−0.253(1)
C131	0.0624(9)	0.0259(8)	0.3552(8)	F3	−0.007(2)	−0.012(2)	−0.103(2)
C132	−0.003(1)	−0.093(1)	0.3445(9)	F4	0.084(3)	−0.050(3)	−0.155(3)
C133	0.052(1)	−0.130(1)	0.287(1)	F5	−0.024(2)	0.050(2)	−0.264(2)
C134	0.157(1)	−0.037(1)	0.262(1)	F6	0.142(2)	0.103(2)	−0.164(2)
C135	0.161(1)	0.059(1)	0.304(1)	OW1	0.3310(6)	−0.3793(6)	−0.3576(6)
C136	−0.1217(9)	−0.1093(9)	0.1323(8)	OW2	−0.3157(7)	0.3328(7)	−0.1776(6)
C137	−0.0133(8)	−0.0507(8)	0.0813(7)	OW3	−0.4605(5)	−0.0233(5)	−0.2757(5)
C138	0.0393(8)	0.0570(8)	0.0989(9)	OW4	0.0100(6)	0.4516(5)	−0.2655(5)
C139	−0.031(1)	0.083(1)	0.1584(9)	OW5	−0.4815(5)	0.4659(5)	−0.2655(5)
C140	−0.128(1)	−0.017(1)	0.1766(9)	OW6	0.3508(6)	−0.3414(6)	−0.1788(6)
P1	0.0351(3)	0.0034(3)	−0.2046(3)	OW7	−0.3363(7)	0.2984(7)	−0.3558(6)
F1	0.095(1)	0.036(1)	−0.302(1)	OW8	−0.362(1)	0.309(1)	0.2386(9)
			CD: Molecule A[a]				
O12	−0.0491(5)	−0.4706(5)	0.2763(5)	C14	−0.2614(6)	−0.4347(6)	0.4192(6)
O13	−0.2581(5)	−0.4689(5)	0.2646(5)	C15	−0.1911(6)	−0.4024(6)	0.5003(6)
O14	−0.2960(5)	−0.3567(5)	0.4068(4)	C16	−0.2562(7)	−0.4169(7)	0.5833(6)
O15	−0.1398(5)	−0.4722(5)	0.5004(4)	C21	0.3460(6)	−0.1302(6)	0.4856(6)
O16	−0.3495(5)	−0.5254(5)	0.5901(5)	C22	0.3274(6)	−0.1983(6)	0.4000(6)
O22	0.4031(5)	−0.1291(5)	0.3359(5)	C23	0.2062(6)	−0.2464(6)	0.3750(6)
O23	0.1869(5)	−0.3097(5)	0.2945(4)	C24	0.1309(6)	−0.3144(6)	0.4480(6)
O24	0.0184(4)	−0.3448(4)	0.4259(4)	C25	0.1574(6)	−0.2497(6)	0.5350(6)
O25	0.2765(4)	−0.1983(4)	0.5504(4)	C26	0.0997(7)	−0.3212(7)	0.6104(6)
O26	0.1232(5)	−0.4117(5)	0.6060(5)	C31	0.4271(6)	0.2881(6)	0.5087(6)
O32	0.5059(5)	0.3194(5)	0.3652(5)	C32	0.4886(7)	0.2576(6)	0.4372(6)
O33	0.4897(5)	0.1045(5)	0.3535(5)	C33	0.4243(6)	0.1322(6)	0.4164(6)
O34	0.3224(4)	−0.0444(4)	0.4721(4)	C34	0.4013(6)	0.0690(6)	0.4964(6)
O35	0.4139(4)	0.2294(4)	0.5813(4)	C35	0.3477(6)	0.1099(6)	0.5685(6)
O36	0.4601(5)	0.1054(5)	0.6799(5)	C36	0.3483(7)	0.0662(7)	0.6536(7)

Atom	x	y	z	Atom	x	y	z
O42	0.1250(5)	0.4172(5)	0.3511(5)	C41	0.0894(6)	0.3641(6)	0.4955(6)
O43	0.3380(5)	0.4104(5)	0.3545(5)	C42	0.1784(6)	0.4174(6)	0.4270(6)
O44	0.3222(4)	0.2621(4)	0.4762(4)	C43	0.2427(6)	0.3523(6)	0.4101(6)
O45	0.1343(5)	0.3594(5)	0.5718(4)	C44	0.2841(6)	0.3406(6)	0.4960(6)
O46	−0.3150(5)	0.4193(5)	0.6774(5)	C45	0.1919(6)	0.2968(6)	0.5648(6)
O52	−0.3033(5)	0.0467(5)	0.2833(4)	C46	0.2334(7)	0.3036(7)	0.6548(6)
O53	−0.0866(6)	0.2495(6)	0.3062(5)	C51	−0.3210(6)	0.0309(6)	0.4347(6)
O54	0.0147(4)	0.2527(4)	0.4610(4)	C52	−0.2656(6)	0.1114(6)	0.3628(6)
O55	−0.2850(5)	0.0870(5)	0.5156(4)	C53	−0.1383(6)	0.1664(6)	0.3677(6)
O56	−0.1448(5)	0.2821(5)	0.6290(5)	C54	−0.1035(6)	0.2184(6)	0.4586(6)
O62	−0.4318(5)	−0.4041(5)	0.2655(5)	C55	−0.1661(6)	0.1338(6)	0.5263(6)
O63	−0.4149(5)	−0.1894(5)	0.2720(5)	C56	0.1399(7)	0.1822(7)	0.6187(7)
O64	−0.2909(5)	−0.0533(4)	0.4203(4)	C61	−0.4105(6)	−0.3884(6)	0.4187(6)
O65	−0.4269(5)	−0.3362(5)	0.4960(4)	C62	−0.4432(7)	−0.3492(7)	0.3419(6)
O66	−0.4831(6)	−0.1803(6)	0.5944(6)	C63	−0.3730(6)	−0.2250(6)	0.3389(6)
C11	−0.0662(7)	−0.4581(6)	0.4313(6)	C64	−0.3777(6)	−0.1676(6)	0.4252(6)
C12	−0.1280(6)	−0.4929(6)	0.3458(6)	C65	−0.3540(7)	−0.2167(7)	0.5010(6)
C13	−0.1897(7)	−0.4291(7)	0.3387(6)	C66	−0.3776(8)	−0.1761(7)	0.5893(7)

CD: Molecule B[a]

Atom	x	y	z	Atom	x	y	z
O12	−0.4844(5)	−0.1075(5)	0.1082(5)	C14	−0.3823(6)	−0.2713(6)	−0.0340(6)
O13	−0.4582(6)	−0.3043(5)	0.1090(5)	C15	−0.3315(6)	−0.1869(6)	−0.1042(6)
O14	−0.3062(4)	−0.3080(4)	−0.0150(4)	C16	−0.3297(7)	−0.2388(7)	−0.1930(6)
O15	−0.3978(5)	−0.1334(5)	−0.1126(4)	C21	−0.0814(6)	0.3346(6)	0.0280(6)
O16	−0.4414(5)	−0.3246(5)	−0.2166(5)	C22	−0.1805(7)	0.2890(7)	0.0930(6)
O22	−0.1483(5)	0.3321(5)	0.1782(5)	C23	−0.2386(7)	0.1613(7)	0.0869(6)
O23	−0.3392(6)	0.1217(6)	0.1414(5)	C24	−0.2699(6)	0.1158(6)	−0.0042(6)
O24	−0.3056(4)	−0.0008(4)	−0.0028(4)	C25	−0.1667(7)	0.1714(7)	−0.0654(6)
O25	−0.1206(5)	0.2901(5)	−0.0549(5)	C26	−0.1977(7)	0.1360(7)	−0.1587(7)
O26	−0.2906(6)	0.1469(6)	−0.1797(5)	C31	0.3373(7)	0.4156(7)	0.0353(6)
O32	0.3512(6)	0.4683(6)	0.1877(5)	C32	0.3037(7)	0.4718(7)	0.1095(6)
O33	0.1418(5)	0.4682(5)	0.1858(5)	C33	0.1749(7)	0.4075(7)	0.1229(6)
O34	−0.0001(5)	0.3097(5)	0.0534(4)	C34	0.1173(6)	0.3925(6)	0.0388(6)
O35	0.2868(5)	0.4184(5)	−0.0396(5)	C35	0.1665(7)	0.3509(7)	−0.0374(6)

Table II. (Contd.)

Atom	x	y	z	Atom	x	y	z
				CD: Molecule B[a]			
O36	0.1448(6)	0.4715(6)	−0.1338(5)	C36	0.1317(8)	0.3624(8)	−0.1254(7)
O42	0.4097(6)	0.0756(6)	0.1873(5)	C41	0.4101(7)	0.0753(7)	0.0333(6)
O43	0.3853(6)	0.2692(6)	0.2022(5)	C42	0.4319(7)	0.1440(7)	0.1173(7)
O44	0.3008(5)	0.3045(5)	0.0546(5)	C43	0.3609(7)	0.1990(7)	0.1247(6)
O45	0.4305(5)	0.1414(5)	−0.0365(4)	C44	0.3809(7)	0.2665(7)	0.0457(6)
O46	0.4958(6)	0.3451(6)	−0.1214(5)	C45	0.3603(6)	0.1908(6)	−0.0371(6)
O52	0.0789(5)	−0.3921(5)	−0.1113(5)	C46	0.3866(7)	0.2503(7)	−0.1200(7)
O53	0.2820(6)	−0.1799(5)	0.1458(5)	C51	0.0883(6)	−0.3398(6)	−0.0340(6)
O54	0.2974(4)	−0.0127(4)	0.0371(4)	C52	0.1512(7)	−0.3203(7)	0.0459(6)
O55	0.1606(5)	−0.2720(5)	−0.0981(4)	C53	0.2062(7)	−0.1994(7)	0.0785(6)
O56	0.3782(6)	−0.1296(5)	0.1544(5)	C54	0.2724(7)	−0.1245(7)	0.0070(6)
O62	−0.3746(5)	0.4733(5)	0.0989(5)	C55	0.2125(7)	−0.1548(6)	−0.0783(6)
O63	−0.1532(5)	0.4554(5)	0.1071(5)	C56	0.2923(6)	−0.1027(6)	−0.1530(6)
O64	0.0023(4)	−0.3114(4)	−0.0123(4)	C61	−0.3304(6)	−0.4164(6)	−0.0474(6)
O65	−0.2638(4)	−0.4114(4)	−0.1201(4)	C62	−0.3064(6)	−0.4682(6)	0.0261(6)
O66	−0.1276(5)	−0.4686(5)	−0.2190(5)	C63	−0.1809(6)	−0.4007(6)	0.0462(6)
C11	−0.4103(6)	−0.0793(6)	−0.0360(6)	C64	−0.1114(6)	−0.3915(6)	−0.0354(6)
C12	−0.4715(7)	−0.1631(7)	0.0331(6)	C65	−0.1447(6)	−0.3479(6)	−0.1084(6)
C13	−0.4033(7)	−0.2178(7)	0.0502(6)	C66	−0.0921(7)	−0.3564(7)	−0.1952(6)

[a] The first digit specifies the glucose residue, the second one the atom number in the glucose ring.

means of intermolecular hydrogen bonding across the secondary hydroxyl faces of adjacent α-CD monomers. The dimers are stacked along the crystallographic c axis forming parallel channels in which the guest cations and anions are lined up alternately. The metallocenium cation is encapsulated within the cavity of the dimer, while the PF_6^- anion is located outside the cavity, being centered between the primary hydroxyl faces of adjacent dimers (Figures 1 and 2). Eight water molecules of hydration per asymmetric unit reside in the spaces between the α-CD columns. On account of the almost identical crystal data a similar structure can be assumed for the α-CD: cobaltocenium adduct **2**.

The bond distances and angles of the cyclodextrin molecules are in good agreement with those found in other cyclodextrin inclusion complexes. In **1** as well as in **3** both α-CD rings are slightly elliptically distorted, the difference in the longest and shortest diagonal distances, which are measured between the glycosidic oxygen atoms, being 0.35 Å and 0.22 Å in **1** and 0.32 Å and 0.18 Å in **3**, respectively. A more convenient measure to compare the van der Waals diameter of cyclodextrin molecules in the O(2)—O(3) region is the tilt angle, which is defined as the angle between the plane through the six glycosidic oxygen atoms and the plane through the O(4)*, C(1), C(4) and O(4) atoms of each glucose residue. As all glucose units incline with their O(6) side turning to the inside of the macrocycle, larger tilt angles make the O(2)—O(3) side of the macrocyclic ring wider. The average tilt angle of cyclodextrin A is 11.8° in **1** and 12.4° in **3** and of cyclodextrin
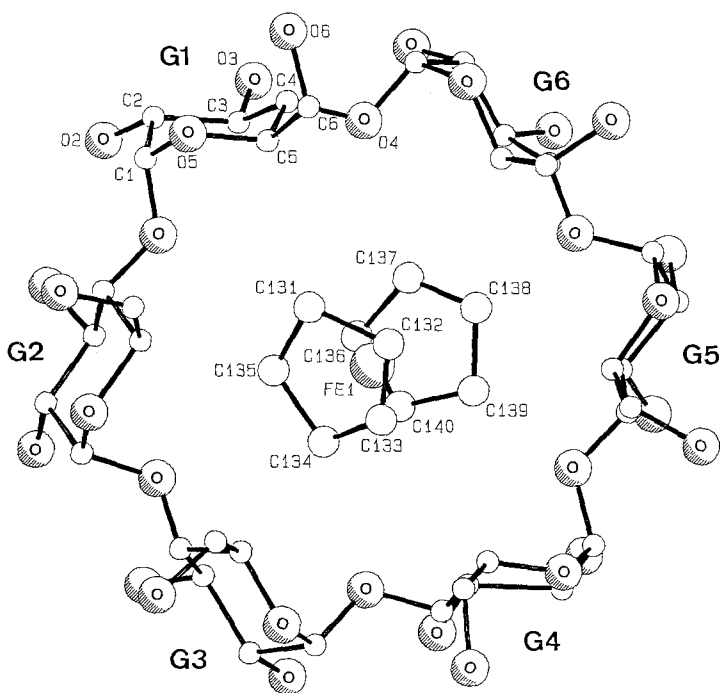

Fig. 1.   A plan view of the ferrocenium cation and of cyclodextrin molecule A in the crystal of **1**. The atomic numbering scheme in **3** is identical.
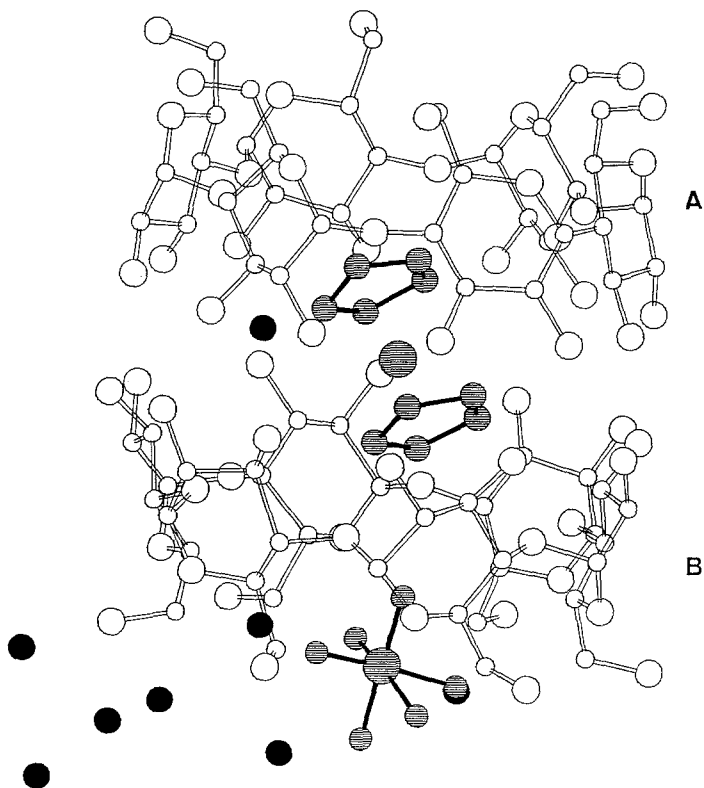
Fig. 2. A side-on view of the skeletal representation of 1 (Guest molecules are hatched, water molecules are shown by black circles).

B 15.3° in **1** and 15.1° in **3**. These differences in the average tilt angles between the two cyclodextrin molecules of a dimer could be observed in all structures with this kind of packing [6, 11] even though the cyclodextrins accommodate different guest molecules. Geometrical data for the α-CD molecules are summarized in Table III.

The guest cation is tilted against the mean planes of the oxygen atoms of the twelve secondary hydroxy groups of α-CD molecules A and B by an angle of 40° and 42/43° in **1** and **3**, respectively [12]. In the crystal of **1**, the iron atom is located almost exactly in the middle between the mean planes of CD A and B, and three carbon atoms of Cp(1) are located inside the cavity of CD A whereas only two atoms of Cp(2) are inserted into CD B. In contrast, the distances of 1.37 and 1.11 Å, respectively of the rhodium atom to the mean planes of CD A and CD B in **3** clearly indicate that the guest molecule is deeper inserted into CD B, and now two atoms of Cp(1) and three atoms of Cp(2) are inserted into CD A and B, respectively. The host guest interactions are governed by van der Waals contacts. The shortest distances are given in Table IV. It is also noteworthy that in both structures in the cavity of CD B there are contacts between a fluorine atom of the PF_6^- anion and two carbon atoms of Cp(2) as indicated as broken lines in Figure 3.

Table III.   Geometrical data for α-cyclodextrin molecules

Compound	1		3	
Cyclodextrin	A	B	A	B
O(4)—O(4) distances (Å)				
O(4,G1)—O(4,G4)	8.32(5)	8.42(5)	8.60(1)	8.48(1)
O(4,G2)—O(4,G5)	8.48(5)	8.64(5)	8.28(1)	8.43(1)
O(4,G3)—O(4,G6)	8.67(5)	8.56(5)	8.46(1)	8.61(1)
Tilt angles (deg)				
G1	13(1)	18(1)	11.8(3)	14.9(6)
G2	12(2)	19(2)	10.4(4)	15.2(4)
G3	13(1)	10(1)	14.5(6)	20.9(2)
G4	7(1)	16(1)	15.3(5)	10.8(3)
G5	13(2)	12(2)	7.9(5)	15.2(4)
G6	13(2)	17(2)	14.3(2)	13.3(5)

Table IV.   Geometry of the guest-host interactions

Distances of the Cp ring atoms from the mean planes of the twelve secondary hydroxy oxygen atoms of CD A and CD B respectively

	CD A of 1	CD A of 3		CD B of 1	CD B of 3
C131	− 0.28(7)	− 0.62(1)	C136	− 0.69(5)	− 0.04(1)
C132	− 0.92(7)	− 0.63(1)	C137	0.18(6)	− 0.98(1)
C133	− 0.72(6)	0.29(1)	C138	0.83(4)	− 0.88(1)
C134	0.37(5)	0.88(1)	C139	0.51(5)	0.06(1)
C135	0.51(7)	0.32(1)	C140	− 0.45(7)	0.54(1)
Me1	1.24(0)	1.37(0)	Me1	1.22(0)	1.11(0)

Host-guest distances < 3.5 Å in 1

C133—C(3,G4,CD A)	3.28(5)
C133—O(4,G4,CD A)	3.41(6)
C137—C(3,G5,CD B)	3.20(7)
C137—O(4,G5,CD B)	3.32(5)
C138—C(3,G5,CD B)	3.47(6)
C139—O(3,G5,CD A)	3.48(6)
C140—O(3,G3,CD B)	3.41(6)
C136—F6	3.29(7)
C140—F6	3.47(5)

Host-guest distances < 3.5 Å in 3

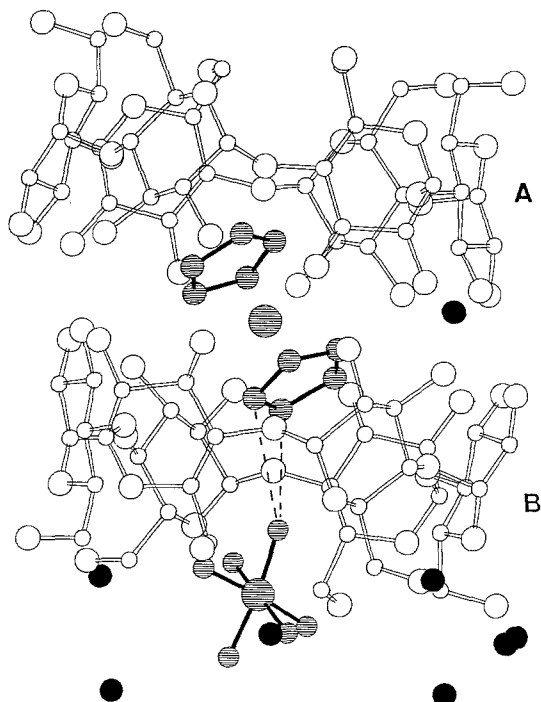|	
C134—O(2,G4,CD B)	3.21(2)
C135—O(3,G4,CD B)	3.42(1)
C136—O(4,G1,CD B)	3.46(1)
C139—O(3,G5,CD A)	3.46(2)
C140—O(2,G5,CD A)	3.29(2)
C137—F3	2.95(3)
C138—F3	3.22(3)

Fig. 3.   A side-on view of the framework representation of **3**.

The geometry of the guest complex in **1** is essentially the same as that observed in uncomplexed ferrocenium salts [13]. The cyclopentadienyl rings are almost eclipsed and are inclined at 3.6° to each other. The average Fe—C(ring) and C—C(ring) distances of 2.12 (4) and 1.48 (5) Å, respectively, and the Fe—ring center distances of 1.67 (4) and 1.72 (4) Å are in agreement with values reported for other ferrocenium salts [13].
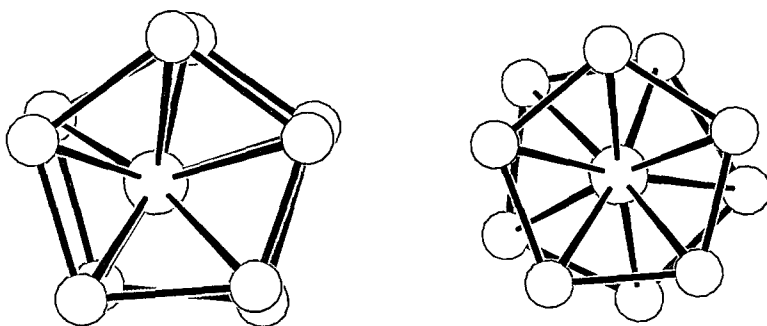

Fig. 4.   Projection of the ferrocenium cation of **1** (left) and the rhodocenium cation of **3** (right) on the plane through Cp(1) [C(131) to C(135)] showing the eclipsed and twisted conformation of the two Cp-rings, respectively.

In the guest cation of **3** the Cp rings are inclined at 1° to each other and are twisted by an angle of 29°. The average Rh—C(ring) and C—C(ring) distances are 2.174 (3) Å and 1.424 (5) Å respectively and in good agreement with the values reported for $[Rh\{\eta^5\text{-}C_5H_2(CO_2Me)_3\}_2][C_5(CO_2Me)_5]$ [14]. The distance between the centers of the rings is 3.61 Å, 0.2 Å longer than that of the guest molecule of **1**, and it appears that the rhodocenium cation seems to fit better into the cavity of the cyclodextrin dimer than the ferrocenium cation (Figure 4).

In conclusion, we have shown that cationic sandwich complexes of the type $[Cp_2M]^+$ (M = Fe, Co, Rh) can be accommodated in the cavity formed by two α-cyclodextrin molecules in channel type structures. The exact orientation of the guest molecule in the cavity depends on the size of the central metal atom and/or the conformation of the ring ligands relative to one another, whereas the structure of the guest complex appears to be unaffected by inclusion into the CD cavity.

Acknowledgement

Notes and References

1. H. M. Colquhoun, J. F. Stoddart, and D. J. Williams: *Angew. Chem.* **98**, 483 (1986); *Angew. Chem. Int. Ed. Engl.* **25**, 487 (1986).
2. Review: J. F. Stoddart and R. Zarzycki: *Recl. Trav. Chim. Pays-Bas* **107**, 515 (1988).
3. (a) A. Harada and S. Takahashi: *J. Chem. Soc., Chem. Commun.* 645 (1984); (b) A. Harada, Y. Hu, S. Yamamoto, and S. Takahashi: *J. Chem. Soc., Dalton Trans.* 729 (1988).
4. (a) F. M. Menger and M. J. Sherrod: *J. Am. Chem. Soc.* **110**, 8606 (1988); (b) M. J. Sherrod: *Carbohydrate Research* **192**, 17 (1989).
5. *Note added in proof*: After submission of this paper the crystal structure analysis of the 2:1 α-CD: ferrocene adduct was published (Y. Odagaki, K. Hirotsu, T. Higuchi, A. Harada, and S. Takahashi: *J. Chem. Soc., Perkin Trans. I.* 1230 (1990)). This structure is isomorphous to the 2:1 α-CD adduct of the ferrocenium salt we report here. It is noteworthy that the two Cp-rings of the guest molecule in the structure reported by Hirotsu *et al.* adopt a staggered arrangement, whereas we observe a nearly eclipsed conformation similar to that of free ferrocene. The calculated model [4] detects essentially no energy difference between eclipsed and staggered ferrocene.
6. B. Klingert and G. Rihs: *Organometallics* **9**, 1135 (1990).
7. D. M. Duggan and D. N. Hendrickson: *Inorg. Chem.* **14**, 955 (1975).
8. J. E. Sheats, W. C. Spink, R. A. Nabinger, D. Nicol, and G. Hlatky: *J. Organomet. Chem.* **251**, 93 (1983).
9. P. T. Beurskens, W. P. Bosman, H. M. Doesburg, R. O. Gould, Th. E. M. van den Hark, P. A. J. Prick, J. H. Noordik, G. Beurskens, V. Parthasarathi, H. J. Bruins Slot, R. C. Haltiwanger, and J. M. M. Smits: *An automatic procedure for phase extension and refinement of difference structure factors*; *Version 1984*.
10. (a) V. I. Sokolov, V. L. Bondareva, and I. F. Golovaneva: *Metalloorg. Khim.* **1**, 716 (1988); (b) V. I. Sokolov, V. L. Bondareva, and I. F. Golovaneva: *J. Organomet. Chem.* **358**, 401 (1988).
11. M. Noltemeyer and W. Saenger: *J. Am. Chem. Soc.* **102**, 2710 (1980).
12. These angles agree well with the values found of the corresponding angles in the crystal structure (42°, [5]) and the docking calculations (~45°, [4]) of the ferrocene adduct.
13. (a) N. J. Mammano, A. Zalkin, A. Landers, and A. L. Rheingold: *Inorg. Chem.* **16**, 297 (1977); (b) E. F. Paulus and L. Schäfer: *J. Organomet. Chem.* **144**, 205 (1978); (c) M. R. Churchill, A. G. Landers, and A. L. Rheingold: *Inorg. Chem.* **20**, 849 (1981).
14. M. I. Bruce, J. R. Rodgers, and J. K. Walton: *J. Chem. Soc., Chem. Commun.* 1253 (1981).