# Molecular Encapsulation of Transition Metal Complexes in Cyclodextrins. Part 3.[1] Structural Consequences of varying the Guest Geometry in Channel-type Inclusion Compounds†

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Inclusion compounds of a range of cyclopentadienyl(arene)iron(II) sandwich complexes, structurally related ferrocenes and (tetramethylcyclobutadiene)cobalt complexes with α-, β- or γ-cyclodextrin (α-, β-, γ-cd) have been prepared. Complexes bearing sterically demanding ring ligands were selectively included in β- or γ-cd. X-Ray crystallographic studies of seven new α-cd adducts demonstrate that the molecular packing of the α-cd macrocycles in channel-type structures depends on the size and shape of the guest complexes. Crystal structure determinations of two of the β-cd adducts reveal a channel-type structure similar to that of the corresponding α-cd adducts, although in these cases the exact orientation of the guest molecules could not be determined due to disorder.

Macrocyclic ligands play an important role in the second-sphere co-ordination of transition-metal complexes. Synthetic molecular receptors of the crown ether type were shown to be ideal hosts for complexes bearing ligands with acidic hydrogen atoms, notably aqua and ammine ligands.[2] Since the first report on the adduct formation between ferrocene and β-cyclodextrin (β-cd) in 1975,[3] numerous papers appeared in the literature describing α-, β- or γ-cyclodextrins as molecular receptors for complexes bearing hydrophobic ligands.[4] While extensive crystallographic studies provide a clear picture of the non-covalent bonding of crown ethers to the first co-ordination sphere of transition-metal complex substrates,[2] there is relatively little structural information on cyclodextrin inclusion compounds with this type of guest molecule. In most cases adduct formation has been proposed on the basis of analytical data and spectroscopic measurements. These methods, however, are insufficient to determine the exact orientation of a guest molecule in the host cavity, and do not supply detailed information on the molecular packing in the crystal.

Recently we reported the synthesis and X-ray crystal structure of the inclusion compound $[Fe(cp)(C_6H_6)]PF_6\cdot2\alpha\text{-cd}\cdot8H_2O$ (cp = $\eta^5$-$C_5H_5$) which, in addition, has been fully characterised by elemental analysis, UV/VIS absorption, induced circular dichroism, and solid-state cross-polarisation magic angle spinning (CP MAS) $^{13}C$ NMR spectroscopy.[5] In subsequent studies, 2:1 host:guest adducts between the metallocenes $[M(cp)_2]PF_6$ (M = Fe, Co, or Rh) and α-cd have been prepared and shown to form a series of isomorphous crystals.[1] In these crystals, the α-cd molecules are arranged head-to-head to form a dimer, with *all* secondary hydroxy groups of one macrocycle linked to the adjacent one by direct hydrogen bonds. The dimers are stacked along the crystallographic *c* axis forming parallel channels in which the guest cations and anions are lined up alternately. The cations are encapsulated within the cavity of the dimers, while the $PF_6^-$ anions are located outside the cavity, being centred between the primary hydroxyl faces of adjacent dimers. It is noteworthy that the crystal structure of the neutral α-cd–ferrocene (2:1) inclusion compound has recently been reported to be almost identical, in spite of the absence of the $PF_6^-$ anions.[6] The unsubstituted sandwich complexes examined so far all seem to be small enough not to influence this particular molecular packing of the α-cyclodextrin rings which has also been found in the crystals of the inclusion compound $LiI_3\cdot I_2\cdot2\alpha\text{-cd}\cdot8H_2O$.[7]

In this paper we describe the preparation and properties of cyclodextrin inclusion compounds of iron, ruthenium and cobalt sandwich complexes bearing four- to eight-membered ring ligands, and discuss the observed selectivities and the structural effects produced by variation of the substrate geometry.

## Results and Discussion

*Preparation and Properties of Inclusion Compounds.*—As an extension of the work cited above, three different series of sandwich complexes have been examined as guest molecules for cyclodextrins. First, a range of cyclopentadienyl(arene)iron(II) complexes **1**–**17**, where arene represents a substituted benzene ring, or naphthalene, biphenyl, indan and tetralin (1,2,3,4-tetrahydronaphthalene). This series also includes complexes **18**–**20** bearing the $\eta^5$-co-ordinated thiophene and the $\eta^6$-co-ordinated seven- and eight-membered ring ligands cycloheptatriene and cyclooctatetraene, respectively. To elucidate the influence of the anion on adduct formation we have also studied the trifluoromethanesulphonate and perfluorobutanesulphonate salts of the cumene complex **6**. The ruthenium analogue of the parent compound of this type $[Ru(cp)(C_6H_6)]PF_6$ **21** and the structurally related, but neutral cyclohexadienyl complex $[Fe(cp)(\eta^5\text{-}C_6H_7)]$ **22** complete the list of complexes bearing an unsubstituted cyclopentadienyl ligand. A second set of guest molecules comprises iron sandwich complexes with substituted cyclopentadienyl ligands, *i.e.* methyl- and pentamethyl-cyclopentadienyl, and both benzene and substituted arenes as second ring ligand. As further examples of disubstituted sandwich complexes 1,1′-dimethylferrocene **27** and the related bridged derivative 1,1′-trimethyleneferrocene **28** as well as its hexafluorophosphate salt **29** have been examined. Finally, adduct formation of the cyclodextrins with the isocobaltocenium salts $[Co(C_4Me_4)(arene)]PF_6$ **30**–**34**, bearing the four-membered tetramethylcyclobutadiene ring ligand, has been studied.

Generally, the inclusion compounds described below were prepared by cocrystallisation of the ionic sandwich complexes with the cyclodextrins from hot aqueous solutions. Upon slow cooling to room temperature the α-cd adducts separated as nice, uniform hexagonal prisms, while the β-cd adducts yielded

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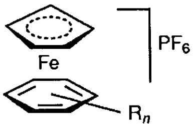
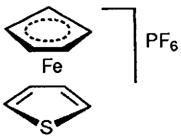
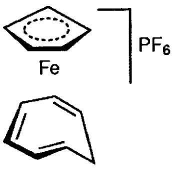
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



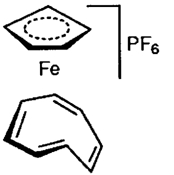
**1** Fluorobenzene
**2** Chlorobenzene
**3** Aniline
**4** Anisole
**5** Toluene
**6** Cumene
**7** Butylbenzene
**8** *sec*-Butylbenzene
**9** *o*-Xylene
**10** *m*-Xylene
**11** *p*-Xylene
**12** Mesitylene
**13** Hexamethylbenzene
**14** Biphenyl
**15** Indan
**16** Tetralin
**17** Naphthalene

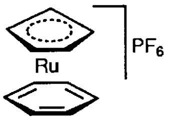


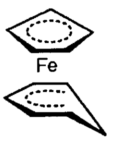
**18**



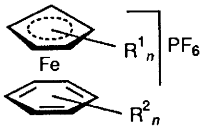
**19**



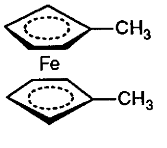


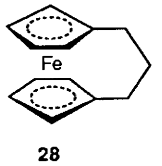


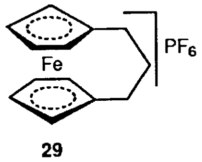
**20** **21** **22**



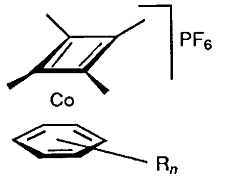
| | $R^1_n$ | $R^2_n$ |
|---|---|---|
| **23** | Me | H |
| **24** | Me | Me |
| **25** | $Me_5$ | H |
| **26** | $Me_5$ | $Me_6$ |







**27** **28** **29**



**30** Benzene
**31** Toluene
**32** *o*-Xylene
**33** Anisole
**34** Aniline

almost exclusively microcrystalline powders. The neutral and water-insoluble guest complexes were added as fine crystals to hot aqueous solutions of the cyclodextrins and the mixtures stirred for several hours; alternatively solvent mixtures were used. The solids which precipitated were filtered off, washed thoroughly with water and ethanol, and then vacuum dried. The host:guest ratio of the products was determined by elemental analysis and $^1$H NMR spectroscopy.

**Table 1** Preparation of 2:1 host:guest inclusion compounds of [Fe(cp)(arene)]$PF_6$ with α- and β-cyclodextrin

| | Yield (%) | | | Yield (%) | |
|---|---|---|---|---|---|
| Guest | α-cd | β-cd | Guest | α-cd | β-cd |
| **1** | 65 | | **11** | 24 | 31 |
| **2** | 32 | | **12** | 72 | 76 |
| **3** | 96 | | **13** | 0 | 67 |
| **4** | 88 | 43 | **14** | 0 | 81 |
| **5** | 63 | | **15** | 68 | 40 |
| **6** | 97 | 77 | **16** | 56 | 62 |
| **7** | 77 | | **17** | 17 | 93 |
| **8** | 6 | 57 | **18** | 30 | 23 |
| **9** | 18 | 55 | **19** | 52 | 24 |
| **10** | 61 | 55 | **20** | 23 | |

**Table 2** Preparation of inclusion compounds of [Fe($C_5H_{5-n}R_n$)(arene)]$PF_6$ and ferrocene derivatives with cyclodextrins

| Guest | Cyclodextrin | Yield (%) | Host:guest molar ratio |
|---|---|---|---|
| **23** | α | 79 | 2:1 |
| **24** | α | 63 | 2:1 |
| **25** | α | 0 | |
| | β | 90 | 2:1 |
| | γ | 0 | |
| **26** | β | 0 | |
| | γ | 48 | 2:1 |
| **27** | α | 80 | 2:1 |
| | β | 95 | 1:1 |
| | γ | 79 | 1:1 |
| **28** | α | 0 | |
| | β | 88 | 1:1 |
| | γ | 71 | 1:1 |
| **29** | α | 23 | 2:1 |
| | β | 36 | 2:1 |

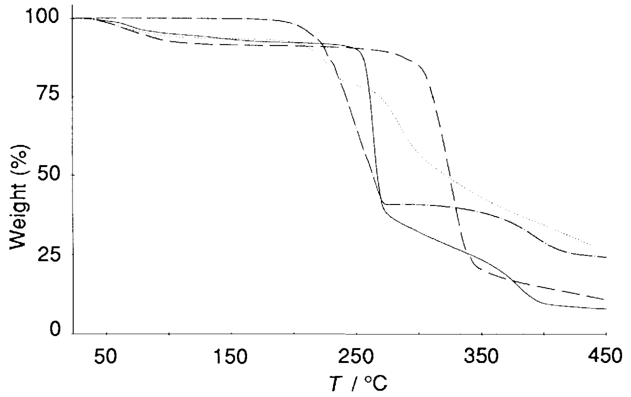


**Fig. 1** Thermogravimetric analysis of [Fe(cp)($C_6H_5Bu$)]$PF_6$ **7** (— • —), its 2:1 α-cd adduct (——), α-cyclodextrin (– – –), and a 1:1 mixture of **7** and α-cyclodextrin (••••)

Table 1 summarises the results on the preparation of inclusion compounds of complexes bearing an unsubstituted cyclopentadienyl ligand. Almost all complexes of this series formed crystalline adducts with α-cyclodextrin. It should be noted that even those bearing a seven- (**19**) or eight-membered ring ligand (**20**) as well as the indan (**15**), tetralin (**16**) or naphthalene complex (**17**) were included. The hexamethylbenzene (**13**) and the biphenyl complex (**14**) are the only guest molecules which are apparently too big to be accommodated into the α-cd cavity. These two derivatives and a selection of the other complexes of this series were subsequently treated with β-cd, and crystalline adducts were obtained in all cases. Attempts to include the mesitylene (**12**), hexamethylbenzene (**13**) and naphthalene complex (**17**) into the larger cavity of γ-cd were unsuccessful; under the conditions applied no crystals separated from the solutions.

The ruthenium complex **21** which is about 10% wider in diameter than its iron analogue afforded an off-white inclusion compound with α-cd in 69% yield. The only neutral guest of this series, the cyclohexadienyl complex **22**, like its ionic precursor $[Fe(cp)(C_6H_6)]PF_6$, readily reacted with α-cd to form an adduct in 55% yield. When the reaction mixture was filtered after stirring for 2 h at 60 °C and the filtrate allowed to cool slowly to room temperature, hair-like needles formed similar to those of the α-cd adduct of ferrocene. Interestingly, the morphology of these crystals is different to that of the comparatively large hexagonal prisms usually obtained with the ionic guest complexes of this series.

A marked effect of the anion on adduct formation was observed using the cumene complex as representative cation. Both, the hexafluorophosphate salt **6** and its trifluoromethanesulphonate formed crystalline adducts with α-cd, however, the yield of the sulphonate salt adduct was much lower (35 *vs.* 97%). Consistent with the increase in size of the anion, the adduct analysed for only 10 instead of 13 water molecules in the crystal. In contrast, the even larger perfluorobutanesulphonate gave no adduct with α-cd at all, but formed an inclusion compound with β-cd quantitatively. According to the analytical data, in all cases stoichiometric 2:1 host:guest adducts were formed with both α- and β-cyclodextrin, and isolated at hydrates.

Of the complexes bearing a substituted cyclopentadienyl ligand (Table 2) both methylcyclopentadienyl derivatives **23** and **24** afforded crystalline adducts with α-cd. The pentamethylcyclopentadienyl complex **25** was selectively included into β-cd which is consistent with the selective inclusion of the structurally very closely related hexamethylbenzene complex **13**. As expected, only γ-cd provides the necessary cavity size to accommodate $[Fe(C_5Me_5)(C_6Me_6)]PF_6$ **26**, the complex bearing two fully methylated ring ligands. As in the first series, the stoichiometry of the isolated adducts is 2:1 host:guest.

Harada and co-workers[8] have reported that α-cd formed 2:1 host:guest complexes with ferrocene and its monosubstituted derivatives, but did not form adducts with 1,1′-disubstituted derivatives. However, circular dichroism spectra of 1,1′-bis(acetyl)ferrocene and two ferrocenophanes in ethylene glycol solutions containing α-cd showed negative induced Cotton effects which indicates inclusion of the chromophores into the chiral cavity of the cyclodextrin at least in solution.[9] The fact that the methylcyclopentadienyl(toluene)iron complex **24** gave an inclusion compound with α-cd therefore led us to investigate adduct formation of the disubstituted ferrocene derivatives **27**–**29**.

Analogous to **24** and ferrocene, 1,1′-dimethylferrocene **27** readily formed a 2:1 host:guest inclusion compound with α-cd, and 1:1 adducts were obtained with both β- and γ-cd. The ferrocenophane **28** formed no adduct with α-cd but gave 1:1 adducts with β- and γ-cd. In contrast, its hexafluorophosphate salt **29** gave 2:1 adducts with both α- and β-cd. These results show that 1,1′-disubstituted sandwich complexes can be accommodated in α-cd and that both the size of the ring substituents and the charge of the complexes affect adduct formation.

The tetramethylcyclobutadiene(arene)cobalt(I) complexes **30**–**34** formed inclusion compounds with β-cyclodextrin selectively. Adducts of 2:1 host:guest stoichiometry were isolated in 46–74% yield. α-Cyclodextrin did not form inclusion compounds with any of the cobalt complexes tested. Apparently, the large tetramethylcyclobutadiene ligand, like the $C_5Me_5$ and the $C_6Me_6$ rings cannot penetrate the α-cd cavity. An attempt to include the *o*-xylene complex **32** into γ-cd failed. Under the conditions applied only starting materials were isolated.

The inclusion compounds obtained are stable in the solid

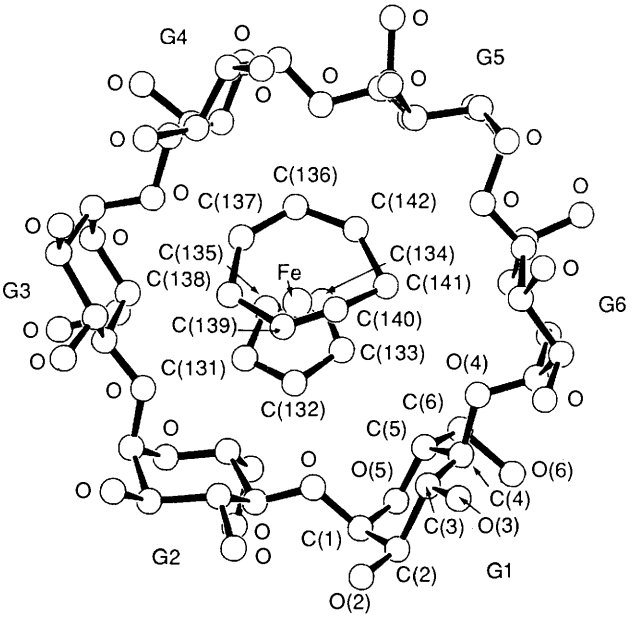


**Fig. 2** Numbering scheme of $[Fe(cp)(\eta^6\text{-}C_7H_8)]^+$ and of cyclodextrin molecule B in the 2:1 α-cd adduct of **19**

**Table 3** Crystal data for the α-cd adducts of packing type I, triclinic, space group *P*1

| | Cell constants | | |
|---|---|---|---|
| Compound | *a*/Å α/° | *b*/Å β/° | *c*/Å γ/° |
| $[Fe(cp)(C_6H_6)]PF_6 \cdot 2\alpha\text{-cd} \cdot 8H_2O$[5] | *a* = 13.815(1)<br>α = 94.23(1) | *b* = 13.929(1)<br>β = 87.15(1) | *c* = 15.639(1)<br>γ = 119.91(1) |
| $[Fe(cp)_2]PF_6 \cdot 2\alpha\text{-cd} \cdot 8H_2O$[1] | *a* = 13.865(2)<br>α = 91.43(2) | *b* = 13.839(2)<br>β = 85.81(2) | *c* = 15.520(2)<br>γ = 120.22(2) |
| $[Co(cp)_2]PF_6 \cdot 2\alpha\text{-cd} \cdot 8H_2O$[1] | *a* = 13.810(2)<br>α = 93.99(2) | *b* = 13.872(2)<br>β = 87.06(2) | *c* = 15.560(2)<br>γ = 120.04(2) |
| $[Rh(cp)_2]PF_6 \cdot 2\alpha\text{-cd} \cdot 8H_2O$[1] | *a* = 13.756(1)<br>α = 94.39(1) | *b* = 13.863(1)<br>β = 86.92(1) | *c* = 15.561(2)<br>γ = 119.89(1) |
| $[Fe(cp)(C_7H_8)]PF_6 \cdot 2\alpha\text{-cd} \cdot 8H_2O$ | *a* = 13.884(2)<br>α = 91.94(2) | *b* = 13.861(2)<br>β = 86.09(2) | *c* = 15.641(2)<br>γ = 120.13(2) |
| $[Fe(cp)(C_8H_8)]PF_6 \cdot 2\alpha\text{-cd} \cdot nH_2O$ | *a* = 13.963(2)<br>α = 90.37(2) | *b* = 13.926(2)<br>β = 90.43(2) | *c* = 16.585(2)<br>γ = 120.25(2) |
| $[Fe(cp)_2] \cdot 2\alpha\text{-cd} \cdot 9H_2O$[6] | *a* = 13.864(5)<br>α = 94.34(7) | *b* = 13.900(6)<br>β = 87.78(6) | *c* = 15.694(9)<br>γ = 120.22(3) |
| $LiI_3 \cdot I_2 \cdot 2\alpha\text{-cd} \cdot 8H_2O$[7] | *a* = 13.38<br>α = 94.1 | *b* = 13.88<br>β = 87.8 | *c* = 15.69<br>γ = 120.0 |

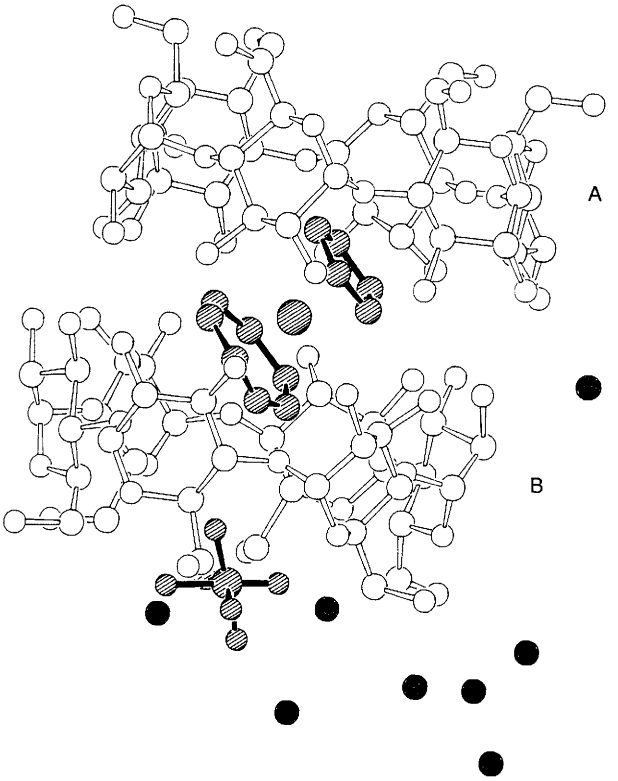


**Fig. 3** Side-on view of the head-to-head type molecular structure of $[Fe(cp)(\eta^6\text{-}C_7H_8)]PF_6{\cdot}2\alpha\text{-cd}{\cdot}8H_2O$. The cation and anion of the guest complex **19** are shaded; water molecules are shown as black circles

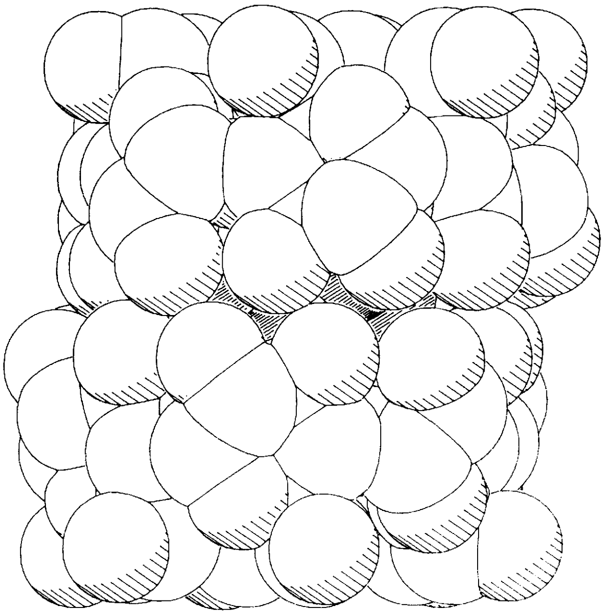


**Fig. 4** Space-filling representation of $[Fe(cp)(\eta^6\text{-}C_7H_8)]^+{\cdot}2\alpha\text{-cd}$ in the crystal of $\mathbf{19}{\cdot}2\alpha\text{-cd}{\cdot}8H_2O$ displaying the complete encapsulation of the guest cation in the 'closed' α-cd dimer

**Table 4** Crystal data for the α-cd adducts of packing type II, trigonal, space group $P3_2$, $Z = 3$, $T = 180 \pm 5$ K

| Compound | $a$/Å | $c$/Å |
|---|---|---|
| $\mathbf{15}{\cdot}2\alpha\text{-cd}{\cdot}13H_2O$ | 13.836(2) | 50.464(4) |
| $\mathbf{6}{\cdot}2\alpha\text{-cd}{\cdot}nH_2O$ | 13.846(2) | 50.272(4) |
| $\mathbf{29}{\cdot}2\alpha\text{-cd}{\cdot}nH_2O$ | 13.812(2) | 50.356(4) |
| $\mathbf{9}{\cdot}2\alpha\text{-cd}{\cdot}nH_2O$ | 13.867(2) | 50.468(4) |
| $\mathbf{4}{\cdot}2\alpha\text{-cd}{\cdot}nH_2O$ | 13.907(2) | 49.700(4) |

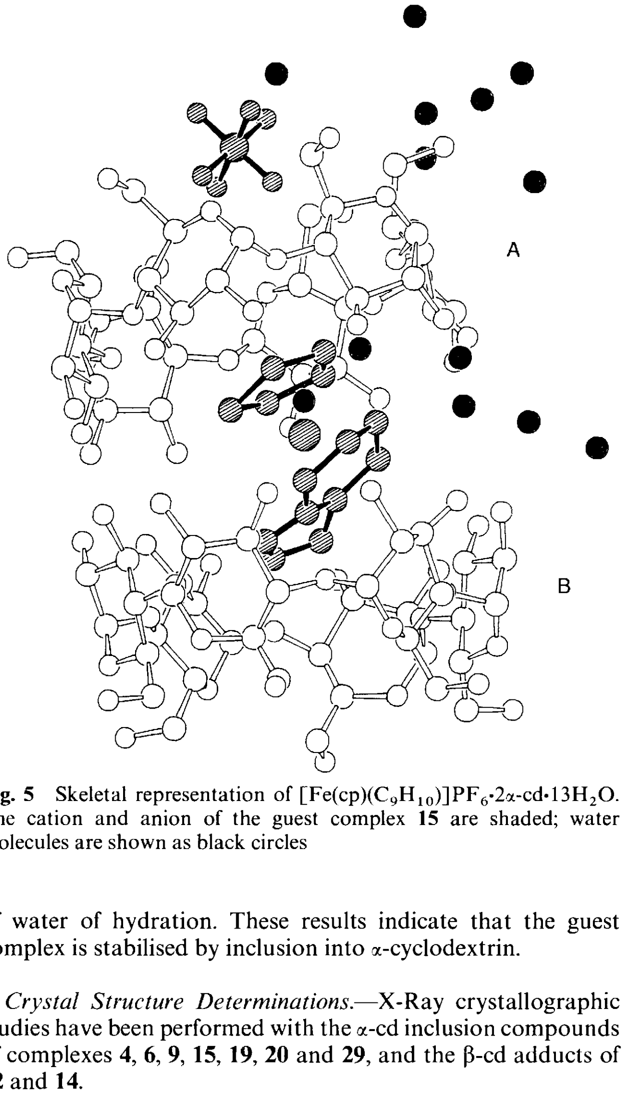


**Fig. 5** Skeletal representation of $[Fe(cp)(C_9H_{10})]PF_6{\cdot}2\alpha\text{-cd}{\cdot}13H_2O$. The cation and anion of the guest complex **15** are shaded; water molecules are shown as black circles

state at ambient conditions for months. Fig. 1 shows the results of the thermogravimeteric analysis of $[Fe(cp)(C_6H_5Bu)]PF_6$ **7**, its 2:1 α-cd adduct, free α-cyclodextrin, and a mixture of α-cd and **7**. In the case of the mixture each component behaved fairly independently, that is the iron complex decomposed slightly above 200 °C and α-cd at around 270 °C. The decomposition of the cyclodextrin in the mixture at a lower temperature compared to free α-cd may be induced by decomposition products of the iron complex. In the case of the inclusion compound there was no change up to 250 °C except for the loss of water of hydration. These results indicate that the guest complex is stabilised by inclusion into α-cyclodextrin.

*Crystal Structure Determinations*.—X-Ray crystallographic studies have been performed with the α-cd inclusion compounds of complexes **4**, **6**, **9**, **15**, **19**, **20** and **29**, and the β-cd adducts of **12** and **14**.

(*a*) *The* α-cd *adducts*. Depending on the geometry of the guest complex two different crystal types of 2:1 α-cd adducts were found. In Table 3 the crystal data for the adducts of **19** and **20** are summarised, and compared with those of isomorphous structures described earlier.[1,5–7] The common feature of these structures is the head-to-head arrangement of two α-cd molecules which are linked together by twelve direct hydrogen bonds between O2(cd A) • • • O3(cd B) and O3(cd A) • • • O2(cd B) forming a closed dimer of defined internal size. These dimers are stacked along the crystallographic $c$ axis to form a channel-type structure. The cd molecules A and B of a dimer are inclined by angles of 3–9° to the stack axis and are shifted laterally to each other by 1.2 Å. Eight water molecules of hydration per asymmetric unit fill the intermolecular spaces between the α-cd columns and are involved in at least four hydrogen bonds. All hydroxyl groups of the cyclodextrins form at least two hydrogen bonds. This particular packing of the α-cd dimer results in a cavity which is large enough to accommodate sandwich complexes bearing unsubstituted five-, six-or seven-membered ring ligands. The numbering scheme is given in Fig. 2, the skeletal representation of the 2:1 α-cd adduct of complex **19** in Fig. 3. The $PF_6^-$ anion is located at the primary hydroxyl side of the α-cd molecule B which encloses the seven-membered ring ligand. Fig. 4 depicts the close contact between the secondary hydroxyl faces of adjacent α-cd monomers. The seven-membered ring is not planar, the $CH_2$ group being bent away from the iron atom and deviating 0.37 Å from the mean plane of the other six rings atoms. Two carbon atoms of the cp ring are located inside the cavity of cd molecule A, and three carbon atoms of the cycloheptatriene ring, including that of the $CH_2$ group, are inserted in cd B. In all structures of the sandwich complex adducts listed in Table 3 the ring ligands of the guest complexes are inclined by angles of 39–47° to the planes through the glycosidic oxygen atoms of the cd rings. The $PF_6^-$ anions of the cationic complexes are located outside the α-cd cavities, being centred between the primary hydroxyl faces of adjacent dimers.

A noticeable change from the above packing description was observed in the packing of the adduct of complex **20**, namely the periodicity along the *c* axis is increased by about 1 Å. The X-ray crystal structure of the free complex reveals that the $\eta^6$-co-ordinated $C_8H_8$ ligand is not planar.[10] The uncomplexed C–C double bond is strongly bent away from the plane of the co-ordinated $C_6$ unit. Therefore, the cyclooctatetraene complex is apparently too large to be encapsulated in the cavity of the fully closed α-cd dimer. Although the morphology of the crystals appeared to be perfect the structure of the adduct could not be solved because of the low intensities of the reflections, pointing to a disorder in the crystal.

A further increase in the size of the guest complexes by introducing various substituents on the ring ligands or bridging the ring ligands as with complex **29** resulted in a substantially different crystal packing. In Table 4 the crystal data for the α-cd adducts of this packing type II are summarised. The structures are isomorphous to each other.

The cyclodextrin molecules are again arranged in a head-to-head manner, but compared to packing type I the dimer is opened up on one side forming an enlarged cavity which can accommodate the larger guest molecules. The cd rings are no longer parallel, but form an angle of 15° to one another. Of the 12 possible direct hydrogen bonds between the secondary hydroxyl groups of the two macrocycles only four were observed. The void created between the rims of the secondary hydroxyl groups by 'opening the molecular capsule' is filled by several water molecules of hydration.

Unfortunately all the guest molecules are disordered, *i.e.* two different positions of the iron atom within the cavity of the dimer could be observed. This may be explained by two different orientations of the guest complex in the cavity in which the cyclopentadienyl ring penetrates either cd molecule A or B. In all cases but one an occupancy of these two positions of 1:1 was found and the remaining atoms of the guest could not be localised. Therefore, the structure analyses of these compounds were not pursued. In the α-cd adduct of the indan ($C_9H_{10}$) complex **15** the occupancy ratio between the two orientations was about 3:1 and the ligand carbon atoms of the major orientation could be localised. Figs. 5 and 6 depict skeletal and space-filling representations of the structure of $[Fe(cp)(C_9H_{10})]PF_6\cdot2\alpha\text{-cd}\cdot13H_2O$. Three carbon atoms of the cp ring are located in the cavity of cd A and the three $CH_2$ groups of the indan ligand are inserted in cd B. The packing of the crystals is shown in Fig. 7. Again, a channel-type structure is formed, however, probably as a result of the angle of 15° between cd molecule A and B of a dimer, adjacent dimers are rotated on the stack axis by an angle of 120° to improve crystal packing. Thus, in contrast to packing type I ($Z = 1$), the unit cell of packing type II contains three α-cd dimers ($Z = 3$). The distance of the iron atom of **15** is 1.3 Å from the three-fold axis. The $PF_6^-$ anions are located between the primary hydroxyl faces of adjacent dimers close to the three-fold axis as well. Thirteen

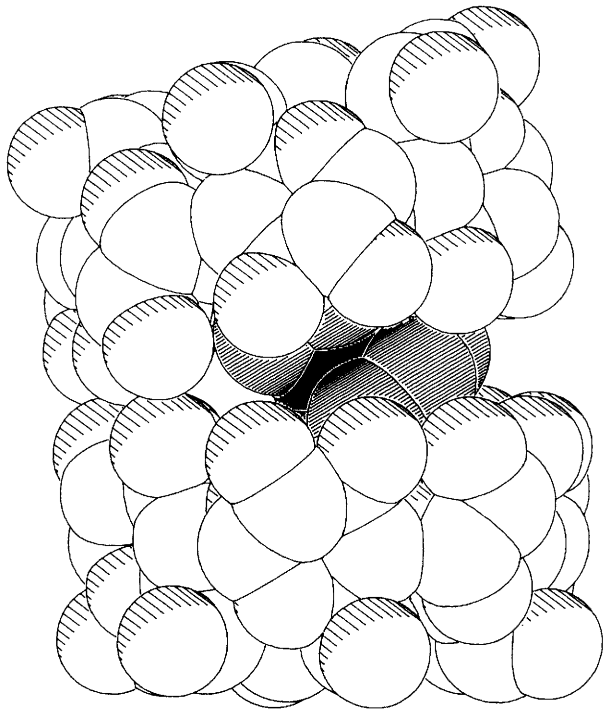


**Fig. 6** Space-filling representation of $[Fe(cp)(C_9H_{10})]^+\cdot2\alpha\text{-cd}$ in the crystal of **15**·2α-cd·13H₂O showing the 'opening' of the α-cd dimer

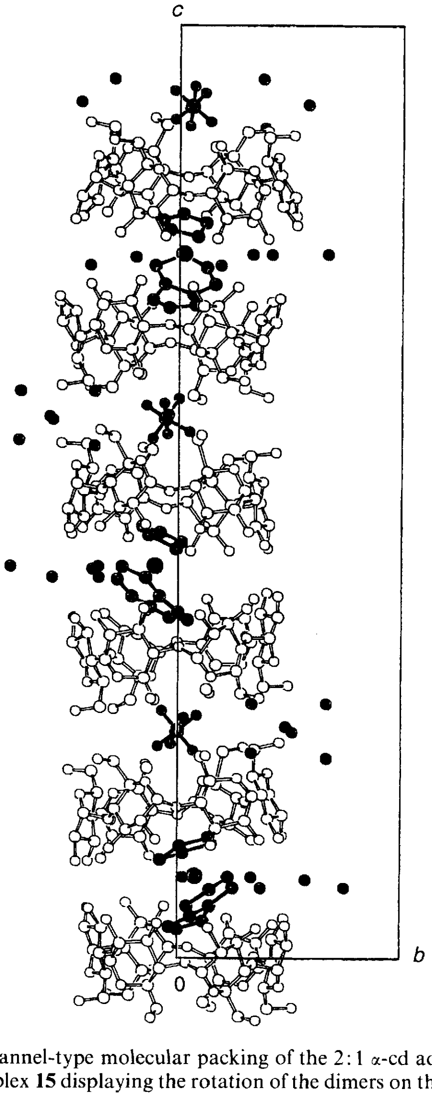


**Fig. 7** Channel-type molecular packing of the 2:1 α-cd adduct of the indan complex **15** displaying the rotation of the dimers on the stack axis

water molecules per dimer are incorporated in the structure linking the cd monomers *via* a hydrogen-bond network. The schematic drawings in Fig. 8 illustrate the differences between the two types of α-cd packing.

(*b*) *The* β-cd *adducts*. The β-cd inclusion compounds of the sandwich complexes examined were usually obtained as microcrystalline powders; only the adducts of **12** and **14** gave crystals suitable for X-ray examination (Table 5). Similar to the related α-cd adducts, the crystal structures of both compounds consist of head-to-head dimers of β-cd molecules which are stacked along the crystallographic *c* axis to form a channel-type structure (Fig. 9). The two β-cd rings of a dimer are linked together by direct hydrogen bonds between the secondary hydroxyl groups and are related by a two-fold axis perpendicular to the stack axis. The iron complex cations are encapsulated within the cavity of the dimer, however they are statistically disordered, so that the carbon atoms of the ligands, the $PF_6^-$ anions and the water molecules could not be localised. The above described packing of the β-cd molecules has already been reported in the literature for adducts of organic guest molecules, and in all cases the guests were disordered.[11]

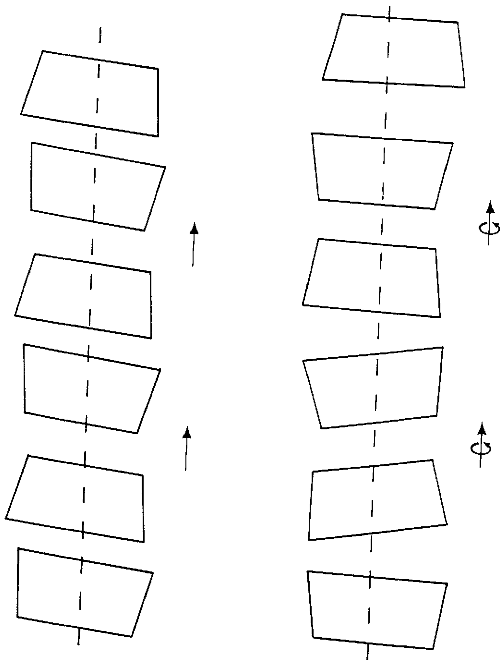


**Fig. 8** Schematic drawings of the packing of α-cyclodextrin in the crystals of packing types I (left) and II (right). Arrows indicate translations and rotations (120°) of the dimers on the stack axis

## Conclusion

A number of transition-metal sandwich complexes of iron, ruthenium and cobalt have been shown to readily form stable inclusion compounds with α-, β- or γ-cyclodextrin. X-Ray crystallographic studies demonstrate the ability of the α-cd molecules as second-sphere ligands to adjust their molecular packing to the size and shape of this type of substrates. Up to a certain size the complexes are included in the closed cavity of an α-cd dimer of packing type I. On increasing the size of the ligands the packing of the cyclodextrins changes significantly in order to accommodate the guests in an enlarged cavity. Complexes bearing both a small and a large ligand may form 1:1 adducts in solution, but the larger ligand hinders a second

**Table 5** Crystal data for the β-cd adducts of complexes **12** and **14**, monoclinic, $Z = 2$, $T = 180 \pm 5$ K

| | Cell constants | | |
|---|---|---|---|
| Compound | $a$/Å $c$/Å | $b$/Å β/° | Space group |
| **12**·2β-cd·$n$H$_2$O | $a = 19.241(2)$ | $b = 24.415(3)$ | $C2$ |
| | $c = 15.768(2)$ | $\beta = 109.55(2)$ | |
| **14**·2β-cd·$n$H$_2$O | $a = 19.206(2)$ | $b = 24.334(3)$ | $P2_1$ |
| | $c = 15.674(2)$ | $\beta = 108.88(2)$ | (pseudo-$C2$) |

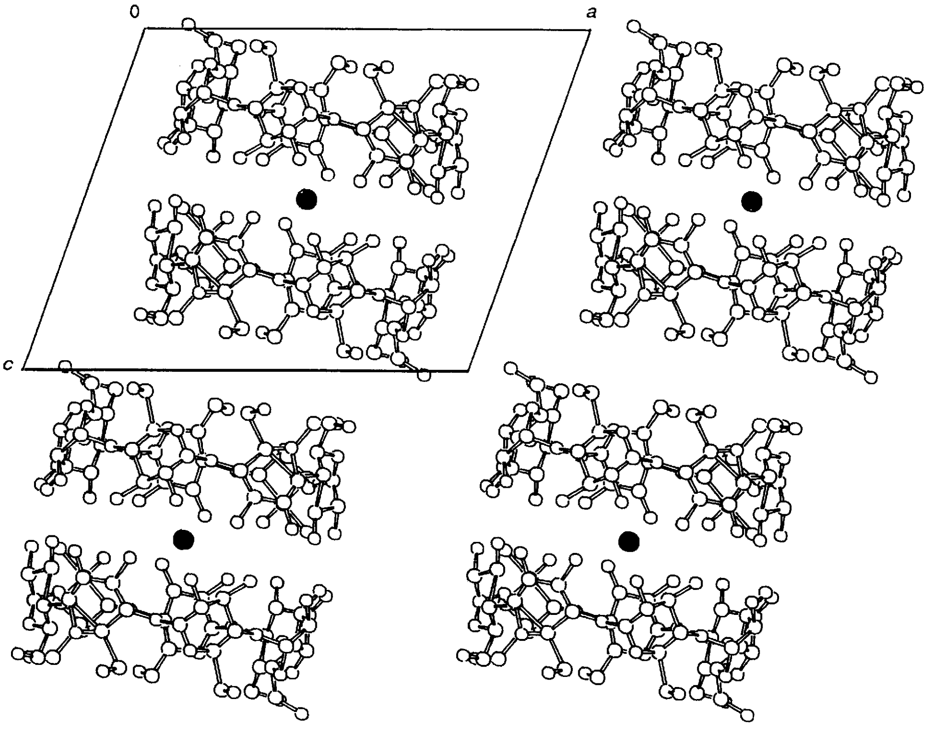


**Fig. 9** Crystal packing of the β-cd adduct of [Fe(cp)($C_6H_3Me_3$-1,3,5)]$PF_6$ **12**. The iron atoms are represented as black circles

Table 6 Analytical data[a] for the inclusion compounds

| | Analysis (%) | | | | | | Analysis (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Adduct | C | H | F | P | M[b] | Adduct | C | H | F | P | M[b] |
| **1**·2α-cd·8$H_2O$ | 40.70 | 6.05 | 5.40 | 1.30 | 2.30 | **17**·2α-cd·14$H_2O$ | 40.35 | 6.30 | 4.45 | 1.20 | 2.15 |
| | (40.65) | (6.00) | (5.40) | (1.25) | (2.30) | | (40.35) | (6.30) | (4.40) | (1.20) | (2.15) |
| **2**·2α-cd·5$H_2O$[c] | 41.45 | 5.85 | 4.70 | 1.30 | 2.30 | **17**·2β-cd·10$H_2O$ | 42.00 | 6.15 | 4.15 | 1.10 | 1.95 |
| | (41.30) | (5.85) | (4.70) | (1.30) | (2.30) | | (41.80) | (6.15) | (4.00) | (1.10) | (1.95) |
| **3**·2α-cd·10$H_2O$[d] | 40.30 | 6.15 | 4.65 | 1.30 | 2.30 | **18**·2α-cd·8$H_2O$[f] | 39.85 | 6.05 | 4.75 | 1.30 | 2.30 |
| | (40.10) | (6.20) | (4.60) | (1.25) | (2.25) | | (39.85) | (6.00) | (4.65) | (1.25) | (2.30) |
| **4**·2α-cd·8$H_2O$ | 40.40 | 6.15 | 4.70 | 1.25 | 2.35 | **18**·2β-cd·5$H_2O$ | 41.20 | 5.95 | 4.15 | 1.10 | 2.05 |
| | (40.95) | (6.10) | (4.65) | (1.25) | (2.25) | | (41.20) | (5.90) | (4.20) | (1.15) | (2.05) |
| **4**·2β-cd·7$H_2O$ | 40.75 | 6.25 | 4.20 | 1.15 | 1.95 | **19**·2α-cd·8$H_2O$ | 41.15 | 6.15 | 4.65 | 1.25 | 2.10 |
| | (41.85) | (6.10) | (4.15) | (1.10) | (2.05) | | (41.20) | (6.15) | (4.65) | (1.25) | (2.30) |
| **5**·2α-cd·6$H_2O$ | 42.10 | 6.00 | 4.75 | 1.25 | 2.05 | **19**·2β-cd·$H_2O$ | 43.10 | 6.05 | 4.55 | 1.25 | 2.15 |
| | (42.40) | (6.00) | (4.70) | (1.25) | (2.30) | | (43.60) | (5.90) | (4.30) | (1.15) | (2.10) |
| **6**·2α-cd·13$H_2O$[e] | 40.20 | 6.45 | 4.40 | 1.15 | 2.00 | **20**·2α-cd·8$H_2O$ | 41.70 | 6.25 | 4.65 | 1.25 | 2.20 |
| | (40.25) | (6.40) | (4.45) | (1.20) | (2.20) | | (41.50) | (6.10) | (4.65) | (1.25) | (2.25) |
| **6**·2β-cd·8$H_2O$ | 41.35 | 6.50 | 4.40 | 1.05 | 1.95 | **21**·2α-cd·7$H_2O$ | 40.45 | 6.10 | 4.65 | 1.25 | 4.10 |
| | (42.05) | (6.25) | (4.05) | (1.10) | (2.00) | | (40.50) | (6.00) | (4.65) | (1.25) | (4.10) |
| **7**·2α-cd·9$H_2O$ | 41.30 | 6.40 | 4.45 | 1.25 | 2.30 | **22**·2α-cd·8$H_2O$ | 43.90 | 6.50 | | | 2.45 |
| | (41.65) | (6.35) | (4.55) | (1.25) | (2.25) | | (43.55) | (6.50) | | | (2.45) |
| **8**·2α-cd·4$H_2O$ | 42.90 | 6.00 | 4.75 | 1.20 | 2.25 | **23**·2α-cd·8$H_2O$ | 41.[illegible] | 6.20 | 4.65 | 1.15 | 2.20 |
| | (43.20) | (6.15) | (4.70) | (1.30) | (2.30) | | (41.20) | (6.15) | (4.65) | (1.25) | (2.30) |
| **8**·2β-cd·6$H_2O$ | 43.45 | 6.25 | 4.30 | 1.20 | 2.10 | **24**·2α-cd·5$H_2O$ | 42.75 | 6.05 | 4.85 | 1.25 | 2.35 |
| | (45.40) | (6.60) | (4.35) | (1.20) | (2.15) | | (42.40) | (6.05) | (4.75) | (1.30) | (2.30) |
| **9**·2α-cd·15$H_2O$ | 40.15 | 6.45 | 4.45 | 1.20 | 2.15 | **25**·2β-cd·16$H_2O$ | 41.1[illegible] | 6.65 | 3.90 | 1.05 | 1.95 |
| | (39.45) | (6.45) | (4.40) | (1.20) | (2.15) | | (40.40) | (6.55) | (3.85) | (1.05) | (1.90) |
| **9**·2β-cd·7$H_2O$ | 42.35 | 6.15 | 4.35 | 1.15 | 2.00 | **26**·2γ-cd·10$H_2O$ | 44.90 | 6.75 | 3.45 | 0.90 | 1.70 |
| | (42.10) | (6.15) | (4.10) | (1.10) | (2.00) | | (43.30) | (6.55) | (3.50) | (0.95) | (1.70) |
| **10**·2α-cd·8$H_2O$ | 41.50 | 6.20 | 4.65 | 1.25 | 2.25 | **27**·2α-cd·6$H_2O$ | 44.50 | 6.50 | | | 2.45 |
| | (41.50) | (6.20) | (4.65) | (1.25) | (2.25) | | (44.45) | (6.35) | | | (2.35) |
| **10**·2β-cd·2$H_2O$ | 42.55 | 6.10 | 4.35 | 1.20 | 2.05 | **27**·β-cd·6$H_2O$ | 45.75 | 6.65 | | | 3.65 |
| | (43.00) | (5.90) | (4.20) | (1.15) | (2.05) | | (44.50) | (6.65) | | | (3.85) |
| **11**·2α-cd·10$H_2O$ | 41.75 | 6.25 | 4.25 | 1.20 | 2.10 | **27**·γ-cd·6$H_2O$ | 45.25 | 6.70 | | | 3.20 |
| | (40.85) | (6.25) | (4.55) | (1.25) | (2.25) | | (44.50) | (6.60) | | | (3.45) |
| **11**·2β-cd·5$H_2O$ | 42.35 | 6.30 | 4.25 | 1.15 | 2.05 | **28**·β-cd·3$H_2O$ | 47.30 | 6.40 | | | 3.95 |
| | (42.65) | (6.10) | (4.15) | (1.15) | (2.05) | | (46.70) | (6.45) | | | (3.95) |
| **12**·2α-cd·12$H_2O$ | 40.20 | 6.35 | 4.45 | 1.25 | 2.20 | **28**·γ-cd·2$H_2O$ | 46.50 | 6.40 | | | 4.00 |
| | (40.55) | (6.40) | (4.45) | (1.20) | (2.20) | | (46.15) | (6.45) | | | (3.65) |
| **12**·2β-cd·6$H_2O$ | 42.70 | 6.15 | 4.35 | 1.15 | 2.05 | **29**·2α-cd·7$H_2O$ | 41.70 | 6.20 | 4.65 | 1.30 | 2.30 |
| | (42.60) | (6.15) | (4.10) | (1.10) | (2.00) | | (41.80) | (6.10) | (4.65) | (1.25) | (2.30) |
| **13**·2β-cd·10$H_2O$ | 42.50 | 6.50 | 3.90 | 1.00 | 1.95 | **29**·2β-cd·5$H_2O$ | 42.55 | 6.05 | 4.50 | 1.20 | 2.35 |
| | (42.15) | (6.40) | (3.95) | (1.05) | (1.95) | | (42.65) | (6.05) | (4.15) | (1.15) | (2.05) |
| **14**·2β-cd·8$H_2O$ | 42.55 | 6.20 | 4.05 | 1.10 | 2.10 | **30**·2β-cd·5$H_2O$ | 42.70 | 6.20 | 4.20 | 1.15 | 2.10 |
| | (42.80) | (6.10) | (4.00) | (1.10) | (1.95) | | (42.80) | (6.20) | (4.15) | (1.15) | (2.15) |
| **15**·2α-cd·13$H_2O$ | 39.95 | 6.35 | 4.45 | 1.20 | 2.20 | **31**·2β-cd·7$H_2O$ | 42.50 | 6.25 | 4.10 | 1.10 | 2.05 |
| | (40.30) | (6.35) | (4.45) | (1.20) | (2.20) | | (42.50) | (6.25) | (4.10) | (1.10) | (2.10) |
| **15**·2β-cd·5$H_2O$ | 42.50 | 6.25 | 4.25 | 1.15 | 2.10 | **32**·2β-cd·3$H_2O$ | 43.60 | 6.25 | 4.65 | 1.20 | 2.30 |
| | (42.90) | (6.05) | (4.15) | (1.15) | (2.05) | | (43.80) | (6.20) | (4.20) | (1.15) | (2.15) |
| **16**·2α-cd·8$H_2O$ | 41.40 | 6.20 | 4.60 | 1.25 | 2.15 | **33**·2β-cd·8$H_2O$ | 42.70 | 6.10 | 3.95 | 1.05 | 2.05 |
| | (42.00) | (6.20) | (4.60) | (1.25) | (2.25) | | (41.95) | (6.25) | (4.00) | (1.10) | (2.10) |
| **16**·2β-cd·6$H_2O$ | 43.15 | 6.20 | 4.25 | 1.10 | 2.05 | **34**·2β-cd·5$H_2O$[g] | 42.60 | 6.15 | 4.10 | 1.10 | 2.10 |
| | (42.85) | (6.15) | (4.10) | (1.10) | (2.00) | | (42.55) | (6.15) | (4.10) | (1.10) | (2.15) |

[a] Calculated values are given in parentheses. [b] M = Fe for **1**–**20** and **22**–**29**, Ru for **21**, and Co for **30**–**34**. [c] Cl, 1.45 (1.45%). [d] N, 0.55 (0.55%). [e] [Fe(cp)($C_6H_5Pr^i$)]$CF_3SO_3$·2α-cd·10$H_2O$: C, 41.60 (41.55); H, 6.30 (6.30); F, 2.25 (2.25); Fe, 2.25 (2.20); S, 1.20 (1.25%). [Fe(cp)($C_6H_5Pr^i$)]-[$C_4F_9SO_3$]·2β-cd·8$H_2O$; C, 41.30 (41.45); H, 6.00 (5.95); F, 5.85 (5.80); Fe, 1.90 (1.90); S, 1.10 (1.10%). [f] S, 1.20 (1.30%). [g] N, 0.50 (0.50%).

Table 7 Crystallographic data

| Guest | **19** | **15** | **12** |
|---|---|---|---|
| Formula | [Fe(cp)($C_7H_8$)]$PF_6$·2($C_{36}H_{60}O_{30}$)·8$H_2O$ | [Fe(cp)($C_9H_{10}$)]$PF_6$·2($C_{36}H_{60}O_{30}$)·13$H_2O$ | [Fe(cp)($C_6H_3Me_3$-1,3,5)]$PF_6$·2($C_{42}H_{70}O_{35}$)·$n$$H_2O$ |
| Crystal size/mm | 0.6 × 0.4 × 0.4 | 0.9 × 0.5 × 0.5 | 0.5 × 0.5 × 0.3 |
| $U$/Å$^3$ | 2597 | 8369 | 6980 |
| $D_c$/g cm$^{-3}$ | 1.565 | 1.526 | |
| μ/cm$^{-1}$ | 23.99 | 22.93 | 4.29 |
| Radiation | Cu-Kα | Cu-Kα | Mo-Kα |
| θ range (°) | 3–60 | 3–60 | 3–26 |
| No. of reflections | 7904 | 9389 | 7294 |
| No. of reflections with $I > 3\sigma(I)$ | 6700 | 7909 | 2234 |
| Final no. of variables | 638 | 669 | 311 |
| Final $R$ | 0.095 | 0.101 | 0.172 |
| $F$(000) | 1292 | 4068 | 2808 |

**Table 8** Fractional atomic coordinates of **19**·2α-cd·8$H_2O$ with estimated standard deviations (e.s.d.s) in parentheses. Glucose residues of cd **A** are numbered 1 to 6, those of cd **B** from 7 to 12. The last digit of the name specifies the atom number of the glucose ring

| Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|
| Guest and water molecules | | | |
| Fe | 0.002 | 0.012 | 0.235 |
| C(131) | 0.099(4) | 0.155(4) | 0.160(3) |
| C(132) | 0.006(4) | 0.146(4) | 0.194(4) |
| C(133) | −0.080(4) | 0.053(4) | 0.154(4) |
| C(134) | −0.041(4) | −0.000(4) | 0.092(3) |
| C(135) | 0.063(4) | 0.062(4) | 0.102(3) |
| C(136) | 0.007(4) | −0.136(4) | 0.249(3) |
| C(137) | 0.103(4) | −0.044(4) | 0.268(3) |
| C(138) | 0.124(4) | 0.053(4) | 0.327(3) |
| C(139) | 0.024(4) | 0.049(4) | 0.371(4) |
| C(140) | −0.071(4) | −0.025(4) | 0.377(4) |
| C(141) | −0.133(4) | −0.095(4) | 0.314(4) |
| C(142) | −0.105(4) | −0.160(4) | 0.273(4) |
| P | 0.022(2) | 0.034(2) | 0.661(1) |
| F(1) | 0.076(4) | 0.093(3) | 0.740(3) |
| F(2) | 0.107(7) | 0.010(7) | 0.661(6) |
| F(3) | −0.063(5) | −0.089(5) | 0.692(4) |
| F(4) | −0.080(5) | 0.035(5) | 0.701(5) |
| F(5) | 0.073(8) | 0.141(7) | 0.639(7) |
| F(6) | −0.05(1) | −0.03(1) | 0.59(1) |
| O(W1) | 0.486(2) | 0.520(2) | 0.726(2) |
| O(W2) | −0.005(2) | 0.535(2) | 0.723(2) |
| O(W3) | 0.648(2) | 0.331(2) | 0.811(2) |
| O(W4) | 0.684(2) | 0.357(2) | 0.638(2) |
| O(W5) | 0.473(2) | 0.011(2) | 0.720(2) |
| O(W6) | 0.352(3) | 0.678(3) | 0.633(2) |
| O(W7) | 0.320(3) | 0.667(3) | 0.815(3) |
| O(W8) | 0.321(3) | 0.639(3) | 0.211(3) |
| cd molecule A | | | |
| O(12) | −0.114(3) | 0.396(3) | 0.104(2) |
| O(13) | −0.293(4) | 0.179(4) | 0.151(3) |
| O(14) | −0.324(2) | 0.010(2) | 0.028(1) |
| O(15) | −0.172(2) | 0.264(2) | −0.101(2) |
| O(16) | −0.383(2) | 0.120(2) | −0.161(2) |
| O(22) | 0.342(3) | 0.489(3) | 0.091(2) |
| O(23) | 0.120(2) | 0.468(2) | 0.104(2) |
| O(24) | −0.021(2) | 0.313(2) | −0.028(2) |
| O(25) | 0.251(2) | 0.410(2) | −0.120(2) |
| O(26) | 0.127(3) | 0.463(3) | −0.209(2) |
| O(32) | 0.437(3) | 0.119(3) | 0.111(2) |
| O(33) | 0.431(2) | 0.327(2) | 0.094(2) |
| O(34) | 0.291(2) | 0.314(2) | −0.032(2) |
| O(35) | 0.387(2) | 0.133(2) | −0.117(2) |
| O(36) | 0.447(2) | 0.316(2) | −0.218(2) |
| O(42) | 0.071(3) | −0.317(3) | 0.168(3) |
| O(43) | 0.282(2) | −0.099(2) | 0.141(2) |
| O(44) | 0.274(2) | 0.004(2) | −0.015(2) |
| O(45) | 0.109(2) | −0.287(2) | −0.066(2) |
| O(46) | 0.298(2) | −0.149(2) | −0.177(2) |
| O(52) | −0.379(2) | −0.432(2) | 0.193(2) |
| O(53) | −0.166(2) | −0.411(2) | 0.183(2) |
| O(54) | −0.034(2) | −0.300(2) | 0.026(2) |
| O(55) | −0.314(2) | −0.431(2) | −0.043(2) |
| O(56) | −0.160(2) | −0.486(2) | −0.142(2) |
| O(62) | −0.450(2) | −0.058(2) | 0.172(2) |
| O(63) | −0.447(2) | −0.264(2) | 0.188(2) |
| O(64) | −0.332(2) | −0.297(2) | 0.039(2) |
| O(65) | −0.450(2) | −0.141(2) | −0.048(2) |
| O(66) | −0.508(2) | −0.353(2) | −0.132(2) |
| C(11) | −0.108(3) | −0.334(3) | −0.036(3) |
| C(12) | −0.179(3) | 0.324(3) | 0.046(3) |
| C(13) | −0.235(4) | 0.195(4) | 0.063(3) |
| C(14) | −0.294(4) | 0.120(4) | 0.009(4) |
| C(15) | −0.224(3) | 0.153(2) | −0.087(2) |
| C(16) | −0.288(3) | 0.098(3) | −0.155(3) |
| C(21) | 0.312(3) | 0.419(3) | −0.048(3) |
| C(22) | 0.277(4) | 0.478(4) | 0.024(3) |
| C(23) | 0.149(3) | 0.406(3) | 0.045(3) |
| C(24) | 0.085(3) | 0.390(3) | −0.042(3) |
| C(25) | 0.138(4) | 0.343(4) | −0.118(3) |
| C(26) | 0.097(3) | 0.357(3) | −0.196(2) |
| C(31) | 0.383(3) | 0.076(3) | −0.041(3) |
| C(32) | 0.442(4) | 0.171(4) | 0.035(4) |
| C(33) | 0.376(4) | 0.236(4) | 0.059(3) |
| C(34) | 0.361(3) | 0.275(3) | −0.041(3) |
| C(35) | 0.321(3) | 0.186(3) | −0.117(3) |
| C(36) | 0.342(3) | 0.234(3) | −0.203(3) |
| C(41) | 0.043(3) | −0.331(3) | 0.015(3) |
| C(42) | 0.133(3) | −0.279(3) | 0.080(3) |
| C(43) | 0.192(4) | −0.155(4) | 0.076(3) |
| C(44) | 0.243(3) | −0.109(3) | −0.009(3) |
| C(45) | 0.149(3) | −0.173(3) | −0.074(3) |
| C(46) | 0.206(3) | −0.133(3) | −0.170(3) |
| C(51) | −0.372(3) | −0.413(3) | 0.032(2) |
| C(52) | −0.329(3) | −0.450(3) | 0.110(2) |
| C(53) | −0.209(3) | −0.375(3) | 0.115(3) |
| C(54) | −0.143(3) | −0.382(2) | 0.030(2) |
| C(55) | −0.196(3) | −0.356(3) | −0.048(3) |
| C(56) | −0.156(3) | −0.383(3) | −0.142(2) |
| C(61) | −0.429(3) | −0.068(3) | 0.018(2) |
| C(62) | −0.478(3) | −0.139(3) | 0.113(3) |
| C(63) | −0.404(3) | −0.189(2) | 0.114(2) |
| C(64) | −0.407(3) | −0.264(3) | 0.033(3) |
| C(65) | −0.381(3) | −0.188(3) | −0.054(3) |
| C(66) | −0.406(3) | −0.262(3) | −0.124(3) |
| cd molecule B | | | |
| O(72) | 0.361(2) | −0.141(2) | 0.284(2) |
| O(73) | 0.146(2) | −0.331(2) | 0.316(2) |
| O(74) | 0.024(2) | −0.300(2) | 0.454(2) |
| O(75) | 0.317(2) | −0.116(2) | 0.506(2) |
| O(76) | 0.168(2) | −0.292(2) | 0.632(2) |
| O(82) | 0.495(2) | 0.355(2) | 0.265(2) |
| O(83) | 0.509(3) | 0.154(3) | 0.274(2) |
| O(84) | 0.341(2) | 0.013(2) | 0.395(2) |
| O(85) | 0.449(2) | 0.287(2) | 0.489(2) |
| O(86) | 0.496(2) | 0.145(2) | 0.591(2) |
| O(92) | 0.102(2) | 0.414(2) | 0.272(2) |
| O(93) | 0.294(2) | 0.392(2) | 0.251(2) |
| O(94) | 0.334(2) | 0.307(2) | 0.403(2) |
| O(95) | 0.166(2) | 0.429(2) | 0.497(2) |
| O(96) | 0.366(2) | 0.488(2) | 0.582(2) |
| O(102) | −0.358(2) | 0.080(2) | 0.340(2) |
| O(103) | −0.145(3) | 0.273(3) | 0.309(2) |
| O(104) | 0.014(2) | 0.299(2) | 0.423(2) |
| O(105) | −0.248(2) | 0.159(2) | 0.552(2) |
| O(106) | −0.108(2) | 0.378(2) | 0.611(2) |
| O(112) | −0.443(2) | −0.370(2) | 0.356(2) |
| O(113) | −0.427(2) | −0.151(2) | 0.347(2) |
| O(114) | −0.288(2) | 0.004(2) | 0.466(2) |
| O(115) | −0.391(2) | −0.265(2) | 0.576(2) |
| O(116) | −0.456(2) | −0.135(2) | 0.666(2) |
| O(122) | −0.086(2) | −0.479(2) | 0.348(2) |
| O(123) | −0.280(2) | −0.445(2) | 0.344(2) |
| O(124) | −0.284(2) | −0.301(2) | 0.471(2) |
| O(125) | −0.108(2) | −0.391(2) | 0.564(2) |
| O(126) | −0.305(3) | −0.447(3) | 0.666(2) |
| C(71) | 0.365(4) | −0.077(4) | 0.430(4) |
| C(72) | 0.309(4) | −0.177(4) | 0.362(4) |
| C(73) | 0.191(3) | −0.230(3) | 0.363(3) |
| C(74) | 0.142(3) | −0.263(3) | 0.457(3) |
| C(75) | 0.199(4) | −0.162(4) | 0.509(3) |
| C(76) | 0.159(4) | −0.191(3) | 0.610(3) |
| C(81) | 0.443(3) | 0.344(3) | 0.411(3) |
| C(82) | 0.499(3) | 0.308(3) | 0.348(3) |
| C(83) | 0.441(4) | 0.182(4) | 0.324(3) |
| C(84) | 0.420(2) | 0.115(2) | 0.413(2) |
| C(85) | 0.379(4) | 0.171(4) | 0.481(3) |
| C(86) | 0.400(3) | 0.141(3) | 0.583(3) |
| C(91) | 0.097(2) | 0.407(2) | 0.424(2) |
| C(92) | 0.183(3) | 0.459(3) | 0.347(3) |

**Table 8** (*continued*)

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* | Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|---|---|---|---|
| C(93) | 0.220(3) | 0.361(3) | 0.330(3) | C(112) | −0.441(3) | −0.302(3) | 0.424(3) |
| C(94) | 0.291(3) | 0.385(3) | 0.411(2) | C(113) | −0.375(3) | −0.180(3) | 0.409(3) |
| C(95) | 0.215(3) | 0.357(3) | 0.495(2) | C(114) | −0.376(3) | −0.112(3) | 0.485(3) |
| C(96) | 0.288(2) | 0.395(2) | 0.578(2) | C(115) | −0.324(3) | −0.141(3) | 0.561(2) |
| C(101) | −0.310(3) | 0.083(3) | 0.488(2) | C(116) | −0.340(4) | −0.094(4) | 0.651(4) |
| C(102) | −0.293(3) | 0.150(3) | 0.407(2) | C(121) | −0.052(4) | −0.409(4) | 0.482(3) |
| C(103) | −0.165(4) | 0.197(4) | 0.380(3) | C(122) | −0.142(3) | −0.462(3) | 0.432(3) |
| C(104) | −0.099(4) | 0.274(4) | 0.449(3) | C(123) | −0.194(3) | −0.390(3) | 0.407(3) |
| C(105) | −0.138(3) | 0.207(3) | 0.538(3) | C(124) | −0.251(3) | −0.381(3) | 0.501(3) |
| C(106) | −0.089(3) | 0.283(3) | 0.610(3) | C(125) | −0.159(3) | −0.325(3) | 0.567(2) |
| C(111) | −0.395(2) | −0.331(2) | 0.504(2) | C(126) | −0.216(4) | −0.324(4) | 0.641(3) |

**Table 9** Fractional atomic coordinates of **15**·2α-cd·13H$_2$O with e.s.d.s in parentheses

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* | Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|---|---|---|---|
| Guest and water molecules | | | | | | | |
| Fe | 0.1032(9) | 0.0804(9) | 0.089 | O(53) | −0.309(2) | 0.224(2) | 0.0434(5) |
| C(131) | 0.040(4) | −0.035(4) | 0.034(1) | O(54) | −0.308(2) | 0.049(2) | 0.0123(5) |
| C(132) | −0.043(4) | 0.000(4) | 0.031(1) | O(55) | −0.148(2) | 0.302(2) | −0.0295(5) |
| C(133) | 0.001(4) | 0.116(4) | 0.040(1) | O(56) | −0.367(2) | 0.156(2) | −0.0519(5) |
| C(134) | 0.082(4) | 0.145(4) | 0.057(1) | O(62) | 0.365(2) | 0.486(2) | 0.0354(6) |
| C(135) | 0.145(4) | 0.250(4) | 0.076(1) | O(63) | 0.151(2) | 0.478(2) | 0.0434(5) |
| C(136) | 0.250(4) | 0.229(4) | 0.088(1) | O(64) | −0.005(2) | 0.347(2) | 0.0023(5) |
| C(137) | 0.271(4) | 0.147(4) | 0.074(1) | O(65) | 0.269(2) | 0.459(2) | −0.0304(5) |
| C(138) | 0.204(4) | 0.043(4) | 0.056(1) | O(66) | 0.120(2) | 0.517(3) | −0.0529(7) |
| C(139) | 0.122(4) | 0.059(4) | 0.045(1) | C(11) | 0.410(3) | 0.117(3) | −0.0151(7) |
| C(140) | 0.133(4) | 0.012(4) | 0.122(1) | C(12) | 0.469(3) | 0.203(3) | 0.0066(7) |
| C(141) | 0.008(4) | −0.076(4) | 0.107(1) | C(13) | 0.404(3) | 0.271(3) | 0.0168(7) |
| C(142) | −0.015(4) | 0.024(4) | 0.114(1) | C(14) | 0.383(3) | 0.309(3) | −0.0135(7) |
| C(143) | 0.080(4) | 0.151(4) | 0.124(1) | C(15) | 0.332(3) | 0.222(3) | −0.0354(8) |
| C(144) | 0.158(4) | 0.139(4) | 0.131(1) | C(16) | 0.346(3) | 0.280(3) | −0.0624(7) |
| P | 0.057(2) | −0.001(2) | 0.2464(6) | C(21) | 0.080(3) | −0.295(3) | −0.0031(8) |
| F(1) | 0.116(5) | 0.071(5) | 0.225(1) | C(22) | 0.179(4) | −0.254(4) | 0.016(1) |
| F(2) | −0.002(4) | −0.070(4) | 0.268(1) | C(23) | 0.237(3) | −0.129(3) | 0.0187(8) |
| F(3) | 0.144(4) | 0.029(4) | 0.261(1) | C(24) | 0.267(3) | −0.075(3) | −0.0110(7) |
| F(4) | −0.049(4) | −0.030(4) | 0.232(1) | C(25) | 0.173(3) | −0.127(3) | −0.0296(7) |
| F(5) | 0.051(5) | −0.088(5) | 0.230(1) | C(26) | 0.210(3) | −0.086(3) | −0.0547(8) |
| F(6) | 0.063(5) | 0.087(5) | 0.263(1) | C(31) | −0.327(3) | −0.370(3) | 0.0083(8) |
| O(W1) | 0.574(2) | −0.003(2) | 0.2479(5) | C(32) | −0.298(3) | −0.409(3) | 0.0333(8) |
| O(W2) | 0.561(2) | 0.513(2) | 0.2448(5) | C(33) | −0.163(3) | −0.338(3) | 0.0328(7) |
| O(W3) | 0.044(2) | 0.484(2) | 0.2505(5) | C(34) | −0.111(3) | −0.343(3) | 0.0051(7) |
| O(W4) | 0.714(2) | 0.330(2) | 0.2226(5) | C(35) | −0.170(3) | −0.314(3) | −0.0170(8) |
| O(W5) | 0.383(2) | 0.576(2) | 0.0849(5) | C(36) | −0.129(3) | −0.323(3) | −0.0432(7) |
| O(W6) | 0.707(2) | 0.332(2) | 0.2754(6) | C(41) | −0.412(3) | −0.035(3) | 0.0123(8) |
| O(W7) | 0.354(2) | 0.750(2) | 0.0762(6) | C(42) | −0.447(3) | −0.107(3) | 0.0344(7) |
| O(W8) | 0.375(2) | 0.666(2) | 0.2168(6) | C(43) | −0.371(3) | −0.158(3) | 0.0383(7) |
| O(W9) | 0.375(2) | 0.666(2) | 0.2754(6) | C(44) | −0.392(3) | −0.231(3) | 0.0111(8) |
| O(W10) | 0.750(2) | 0.082(2) | 0.0879(6) | C(45) | −0.362(3) | −0.152(3) | −0.0135(7) |
| O(W11) | 0.563(2) | 0.375(2) | 0.0759(6) | C(46) | −0.385(3) | −0.213(3) | −0.0398(7) |
| O(W12) | 0.750(2) | 0.332(2) | 0.0884(6) | C(51) | −0.088(3) | 0.369(3) | −0.0096(8) |
| O(W13) | 0.355(2) | −0.975(2) | 0.0879(6) | C(52) | −0.163(3) | 0.357(3) | 0.0167(7) |
| O(12) | 0.467(2) | 0.141(2) | 0.0331(5) | C(53) | −0.225(3) | 0.237(3) | 0.0272(8) |
| O(13) | 0.461(2) | 0.355(2) | 0.0321(5) | C(54) | −0.287(3) | 0.154(3) | 0.0002(7) |
| O(14) | 0.300(2) | 0.340(2) | −0.0061(5) | C(55) | −0.263(4) | 0.192(4) | −0.0235(9) |
| O(15) | 0.403(2) | 0.170(2) | −0.0359(5) | C(56) | −0.284(3) | 0.121(3) | −0.0472(7) |
| O(16) | 0.457(2) | 0.355(2) | −0.0667(6) | C(61) | 0.323(3) | 0.455(3) | −0.0120(7) |
| O(22) | 0.140(3) | −0.313(3) | 0.0414(7) | C(62) | 0.303(3) | 0.495(3) | 0.0146(7) |
| O(23) | 0.329(2) | −0.088(2) | 0.0378(5) | C(63) | 0.174(3) | 0.429(3) | 0.0208(8) |
| O(24) | 0.305(2) | 0.040(2) | −0.0051(5) | C(64) | 0.109(3) | 0.424(3) | −0.0047(7) |
| O(25) | 0.120(2) | −0.246(2) | −0.0291(5) | C(65) | 0.151(3) | 0.396(3) | −0.0314(7) |
| O(26) | 0.287(2) | −0.114(2) | −0.0642(6) | C(66) | 0.107(3) | 0.407(3) | −0.0539(9) |
| O(32) | −0.340(2) | −0.401(2) | 0.0542(5) | O(72) | −0.056(2) | −0.454(2) | 0.1046(5) |
| O(33) | −0.131(2) | −0.394(2) | 0.0536(5) | O(73) | −0.229(2) | −0.398(2) | 0.1048(5) |
| O(34) | 0.004(2) | −0.266(2) | 0.0079(5) | O(74) | −0.258(2) | −0.296(2) | 0.1496(5) |
| O(35) | −0.287(2) | −0.384(2) | −0.0161(5) | O(75) | −0.102(2) | −0.434(2) | 0.1772(5) |
| O(36) | −0.140(2) | −0.434(2) | −0.0468(5) | O(76) | −0.307(2) | −0.488(2) | 0.2036(5) |
| O(42) | −0.449(2) | −0.056(2) | 0.0566(6) | O(82) | 0.429(2) | −0.096(2) | 0.1287(5) |
| O(43) | −0.399(2) | −0.227(2) | 0.0603(6) | O(83) | 0.222(2) | −0.304(2) | 0.1190(5) |
| O(44) | −0.305(2) | −0.263(2) | 0.0134(5) | O(84) | 0.053(2) | −0.307(2) | 0.1501(5) |
| O(45) | −0.432(2) | −0.106(2) | −0.0129(5) | O(85) | 0.302(2) | −0.141(2) | 0.1909(5) |
| O(46) | −0.494(2) | −0.312(2) | −0.0387(5) | O(86) | 0.158(2) | −0.355(2) | 0.2150(6) |
| O(52) | −0.100(2) | 0.431(2) | 0.0369(5) | O(92) | 0.488(2) | 0.369(2) | 0.1287(5) |

**Table 9** (*continued*)

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| O(93) | 0.477(2) | 0.152(2) | 0.1224(5) |
| O(94) | 0.351(2) | −0.003(2) | 0.1640(5) |
| O(95) | 0.458(2) | 0.269(2) | 0.1953(5) |
| O(96) | 0.522(2) | 0.126(2) | 0.2196(6) |
| O(102) | 0.146(2) | 0.470(2) | 0.1328(5) |
| O(103) | 0.350(2) | 0.457(2) | 0.1305(5) |
| O(104) | 0.341(2) | 0.303(2) | 0.1704(5) |
| O(105) | 0.169(2) | 0.404(2) | 0.2008(5) |
| O(106) | 0.348(2) | 0.457(2) | 0.2338(5) |
| O(112) | −0.315(2) | 0.150(2) | 0.1251(6) |
| O(113) | −0.097(2) | 0.332(2) | 0.1283(5) |
| O(114) | 0.039(2) | 0.307(2) | 0.1686(5) |
| O(115) | −0.248(2) | 0.115(2) | 0.1922(5) |
| O(116) | −0.103(2) | 0.295(2) | 0.2287(5) |
| O(122) | −0.401(2) | −0.339(2) | 0.1075(5) |
| O(123) | −0.388(2) | −0.123(2) | 0.1113(5) |
| O(124) | −0.271(2) | 0.004(2) | 0.1556(5) |
| O(125) | −0.380(2) | −0.284(2) | 0.1786(5) |
| O(126) | −0.437(2) | −0.143(3) | 0.2099(5) |
| C(71) | −0.038(3) | −0.417(3) | 0.1567(7) |
| C(72) | −0.115(3) | −0.455(3) | 0.1307(8) |
| C(73) | −0.158(3) | −0.366(3) | 0.1258(7) |
| C(74) | −0.236(3) | −0.378(3) | 0.1533(7) |
| C(75) | −0.147(3) | −0.357(3) | 0.1792(7) |
| C(76) | −0.222(3) | −0.384(3) | 0.2022(8) |
| C(81) | 0.368(3) | −0.086(3) | 0.1724(8) |
| C(82) | 0.359(3) | −0.160(3) | 0.1486(8) |
| C(83) | 0.237(3) | −0.228(3) | 0.1389(7) |
| C(84) | 0.158(3) | −0.282(3) | 0.1616(8) |
| C(85) | 0.184(3) | −0.207(3) | 0.1875(7) |
| C(86) | 0.118(3) | −0.284(3) | 0.2128(8) |
| C(91) | 0.455(3) | 0.335(3) | 0.1762(7) |
| C(92) | 0.493(3) | 0.303(3) | 0.1489(8) |
| C(93) | 0.422(3) | 0.173(3) | 0.1406(7) |
| C(94) | 0.422(3) | 0.109(3) | 0.1691(8) |
| C(95) | 0.384(3) | 0.147(3) | 0.1923(8) |
| C(96) | 0.409(3) | 0.104(3) | 0.2186(8) |
| C(101) | 0.126(3) | 0.414(3) | 0.1782(8) |
| C(102) | 0.201(3) | 0.469(3) | 0.1552(7) |
| C(103) | 0.261(3) | 0.405(3) | 0.1513(7) |
| C(104) | 0.305(3) | 0.380(3) | 0.1778(7) |
| C(105) | 0.222(3) | 0.339(3) | 0.1972(8) |
| C(106) | 0.287(3) | 0.344(3) | 0.2263(8) |
| C(111) | −0.298(3) | 0.079(3) | 0.1692(8) |
| C(112) | −0.252(3) | 0.183(3) | 0.1491(8) |
| C(113) | −0.129(3) | 0.236(3) | 0.1451(7) |
| C(114) | −0.076(3) | 0.269(3) | 0.1740(8) |
| C(115) | −0.129(3) | 0.171(3) | 0.1887(7) |
| C(116) | −0.087(3) | 0.205(3) | 0.2238(8) |
| C(121) | −0.368(3) | −0.336(3) | 0.1560(8) |
| C(122) | −0.406(3) | −0.288(3) | 0.1325(7) |
| C(123) | −0.346(3) | −0.162(3) | 0.1309(8) |
| C(124) | −0.343(3) | −0.111(3) | 0.1604(8) |
| C(125) | −0.316(3) | −0.171(3) | 0.1834(8) |
| C(126) | −0.325(3) | −0.137(3) | 0.2062(7) |

**Table 10** Selected bond lengths (Å) and angles (°) of **19**·2α-cd·8$H_2O$ with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Fe–C(131) | 2.09(4) | C(131)–C(135) | 1.44(7) |
| Fe–C(132) | 1.95(6) | C(132)–C(133) | 1.40(6) |
| Fe–C(133) | 2.03(6) | C(133)–C(134) | 1.44(8) |
| Fe–C(134) | 2.33(6) | C(134)–C(135) | 1.27(6) |
| Fe–C(135) | 2.19(5) | C(136)–C(137) | 1.35(5) |
| Fe–C(136) | 2.11(6) | C(136)–C(142) | 1.45(8) |
| Fe–C(137) | 2.01(6) | C(137)–C(138) | 1.53(8) |
| Fe–C(138) | 2.14(6) | C(138)–C(139) | 1.48(8) |
| Fe–C(139) | 2.18(5) | C(139)–C(140) | 1.20(6) |
| Fe–C(142) | 2.16(4) | C(141)–C(142) | 1.55(9) |
| C(131)–C(132) | 1.31(8) | C(140)–C(141) | 1.46(6) |
| C(132)–C(131)–C(135) | 104(4) | C(136)–C(137)–C(138) | 130(5) |
| C(131)–C(132)–C(133) | 106(5) | C(137)–C(138)–C(139) | 116(4) |
| C(132)–C(133)–C(134) | 114(5) | C(138)–C(139)–C(140) | 130(6) |
| C(133)–C(134)–C(135) | 97(4) | C(139)–C(140)–C(141) | 143(6) |
| C(131)–C(135)–C(134) | 119(5) | C(140)–C(141)–C(142) | 100(4) |
| C(137)–C(136)–C(142) | 127(5) | C(136)–C(142)–C(141) | 138(4) |

**Table 11** Selected bond lengths (Å) and angles (°) of **15**·2α-cd·13$H_2O$ with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Fe–C(134) | 1.95(6) | C(131)–C(132) | 1.45(9) |
| Fe–C(135) | 2.22(6) | C(131)–C(139) | 1.35(6) |
| Fe–C(136) | 2.04(4) | C(132)–C(133) | 1.47(7) |
| Fe–C(137) | 2.17(5) | C(133)–C(134) | 1.31(7) |
| Fe–C(139) | 2.28(5) | C(134)–C(135) | 1.61(7) |
| Fe–C(140) | 2.03(6) | C(134)–C(139) | 1.65(9) |
| Fe–C(141) | 1.86(5) | C(135)–C(136) | 1.73(9) |
| Fe–C(142) | 2.02(6) | C(136)–C(137) | 1.48(9) |
| Fe–C(143) | 1.93(6) | C(137)–C(138) | 1.61(7) |
| Fe–C(144) | 2.25(5) | C(138)–C(139) | 1.42(9) |
| C(140)–C(141) | 1.60(7) | C(140)–C(144) | 1.68(8) |
| C(142)–C(143) | 1.42(6) | C(143)–C(144) | 1.20(9) |
| C(132)–C(131)–C(139) | 99(5) | C(136)–C(137)–C(138) | 139(5) |
| C(131)–C(132)–C(133) | 112(4) | C(137)–C(138)–C(139) | 100(5) |
| C(132)–C(133)–C(134) | 110(6) | C(131)–C(139)–C(134) | 114(5) |
| C(133)–C(134)–C(135) | 131(6) | C(131)–C(139)–C(138) | 111(5) |
| C(133)–C(134)–C(139) | 96(4) | C(134)–C(139)–C(138) | 128(4) |
| C(135)–C(134)–C(139) | 130(5) | C(141)–C(140)–C(144) | 118(5) |
| C(134)–C(135)–C(136) | 100(4) | C(142)–C(143)–C(144) | 119(6) |
| C(135)–C(136)–C(137) | 119(4) | C(140)–C(144)–C(143) | 103(4) |

α-cd molecule from approaching close enough to form a dimer. In the case of transition-metal sandwich complexes, bulky ring ligands as $C_4Me_4$, $C_5Me_5$ or $C_6Me_6$ apparently are too large for inclusion in α-cd and no crystalline adducts are formed.

## Experimental

*Materials.*—Cyclodextrins were obtained from Fluka Chemie and 1,1′-dimethylferrocene from Aldrich and used as received. The guest complexes $[Fe(cp)(\eta^6\text{-}C_7H_8)]PF_6$,[12] $[Fe(cp)(\eta^6\text{-}C_8H_8)]PF_6$,[10] $[Fe(cp)(\eta^5\text{-}C_4H_4S)]PF_6$,[13] $[Fe(cp)(\eta^5\text{-}C_6H_7)]$,[14] $[Fe(C_5Me_5)(arene)]PF_6$,[15] **28**,[16] **29**,[17] $[Ru(cp)(C_6H_6)]PF_6$,[18] and $[Co(C_4Me_4)(arene)]PF_6$,[19] were prepared according to the methods described in the literature. All other complexes of the $[Fe(cp)(arene)]PF_6$ series were prepared by the method of Nesmeyanov and co-workers.[20] The complexes were purified by recrystallisation from acetone–diethyl ether or $CH_2Cl_2$–pentane or by alumina column chromatography with acetone, and their purities verified by elemental analysis and $^1H$ NMR spectra.

*Preparation of the Inclusion Compounds.*—The inclusion compounds were synthesised as described previously for $[Fe(cp)(C_6H_6)]PF_6$·2α-cd·8$H_2O$.[5] Typically, the guest complex (1 mmol) was dissolved in the minimum amount of distilled water at 80 °C [20–50 $cm^3$ for most complexes, up to 250 $cm^3$ for less-soluble derivatives like the indan or tetralin(iron) complex or the cobalt complexes], and a hot solution of α-, β- or γ-cyclodextrin (2.2 mmol) in water (20–30 $cm^3$) was added. After stirring for several minutes at 80 °C the hot mixture was filtered and slowly cooled to room temperature. The products which precipitated were filtered off, washed successively with water and ethanol to remove any remaining cyclodextrin and non-included guest complex, and vacuum dried.

**Table 12** Fractional atomic coordinates of **12**•2β-cd with e.s.d.s in parentheses

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* | Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|---|---|---|---|
| O(12) | 0.451(2) | 0.268 | 0.383(3) | C(15) | 0.609(4) | 0.200(3) | 0.231(5) |
| O(13) | 0.606(3) | 0.237(2) | 0.447(4) | C(16) | 0.541(6) | 0.220(6) | 0.124(8) |
| O(14) | 0.497(2) | 0.212(2) | 0.265(3) | C(21) | 0.440(4) | 0.246(3) | 0.252(6) |
| O(15) | 0.666(2) | 0.205(2) | 0.227(3) | C(22) | 0.406(2) | 0.266(2) | 0.303(3) |
| O(16) | 0.574(2) | 0.281(2) | 0.112(3) | C(23) | 0.365(3) | 0.214(2) | 0.329(4) |
| O(22) | 0.734(3) | 0.197(2) | 0.467(4) | C(24) | 0.311(4) | 0.206(4) | 0.234(6) |
| O(23) | 0.317(3) | 0.217(2) | 0.380(4) | C(25) | 0.344(4) | 0.199(3) | 0.175(6) |
| O(24) | 0.261(2) | 0.148(2) | 0.224(3) | C(26) | 0.294(5) | 0.198(5) | 0.059(7) |
| O(25) | 0.396(3) | 0.246(3) | 0.175(4) | C(31) | 0.184(3) | 0.154(2) | 0.190(4) |
| O(26) | 0.264(3) | 0.250(3) | 0.052(4) | C(32) | 0.150(4) | 0.121(4) | 0.252(6) |
| O(32) | 0.176(3) | 0.159(2) | 0.324(3) | C(33) | 0.176(2) | 0.064(2) | 0.284(3) |
| O(33) | 0.154(2) | 0.048(2) | 0.353(3) | C(34) | 0.167(4) | 0.042(4) | 0.194(5) |
| O(34) | 0.195(2) | −0.015(2) | 0.202(3) | C(35) | 0.199(5) | 0.058(4) | 0.126(7) |
| O(35) | 0.175(3) | 0.117(2) | 0.105(4) | C(36) | 0.166(6) | 0.036(6) | 0.038(8) |
| O(36) | 0.094(3) | 0.041(2) | −0.011(3) | C(41) | 0.135(7) | 0.072(6) | 0.18(1) |
| O(42) | 0.136(3) | −0.070(2) | 0.338(3) | C(42) | 0.159(4) | 0.105(3) | 0.282(5) |
| O(43) | 0.256(2) | −0.153(2) | 0.377(3) | C(43) | 0.238(3) | 0.117(2) | 0.302(4) |
| O(44) | 0.322(3) | −0.163(2) | 0.246(4) | C(44) | 0.239(6) | 0.155(5) | 0.220(8) |
| O(45) | 0.149(3) | −0.097(2) | 0.111(4) | C(45) | 0.226(3) | 0.105(2) | 0.127(4) |
| O(46) | 0.155(4) | −0.193(3) | 0.029(5) | C(46) | 0.225(4) | 0.149(3) | 0.055(5) |
| O(52) | 0.370(3) | −0.230(3) | 0.386(4) | C(51) | 0.365(5) | 0.217(4) | 0.242(7) |
| O(53) | 0.529(3) | −0.220(3) | 0.429(4) | C(52) | 0.412(4) | 0.237(3) | 0.329(5) |
| O(54) | 0.564(4) | −0.189(3) | 0.296(5) | C(53) | 0.481(4) | 0.205(3) | 0.351(5) |
| O(55) | 0.374(4) | −0.213(3) | 0.168(5) | C(54) | 0.479(4) | 0.201(3) | 0.263(6) |
| O(56) | 0.492(5) | −0.237(4) | 0.112(6) | C(55) | 0.444(3) | 0.188(2) | 0.180(4) |
| O(62) | 0.664(3) | −0.216(2) | 0.447(4) | C(56) | 0.461(4) | 0.178(3) | 0.100(5) |
| O(63) | 0.770(2) | −0.111(2) | 0.475(3) | C(61) | 0.616(4) | 0.196(4) | 0.307(6) |
| O(64) | 0.738(4) | −0.048(3) | 0.346(6) | C(62) | 0.691(4) | 0.194(4) | 0.390(6) |
| O(65) | 0.652(3) | −0.177(3) | 0.232(4) | C(63) | 0.694(3) | 0.125(3) | 0.392(4) |
| O(66) | 0.750(4) | −0.140(4) | 0.154(5) | C(64) | 0.727(3) | 0.109(3) | 0.317(4) |
| O(72) | 0.835(3) | −0.016(3) | 0.479(4) | C(65) | 0.664(5) | 0.107(4) | 0.252(6) |
| O(73) | 0.792(2) | 0.086(2) | 0.494(3) | C(66) | 0.697(5) | 0.090(4) | 0.154(7) |
| O(74) | 0.702(3) | 0.134(3) | 0.313(4) | C(71) | 0.786(6) | 0.024(6) | 0.323(8) |
| O(75) | 0.778(4) | 0.015(4) | 0.252(6) | C(72) | 0.819(4) | 0.014(4) | 0.399(5) |
| O(76) | 0.779(4) | 0.113(3) | 0.163(5) | C(73) | 0.773(3) | 0.061(3) | 0.418(4) |
| C(11) | 0.708(4) | 0.196(3) | 0.324(5) | C(74) | 0.760(4) | 0.087(3) | 0.306(6) |
| C(12) | 0.694(3) | 0.212(3) | 0.389(5) | C(75) | 0.728(5) | 0.056(5) | 0.240(7) |
| C(13) | 0.623(4) | 0.211(3) | 0.372(5) | C(76) | 0.731(7) | 0.088(6) | 0.15(1) |
| C(14) | 0.571(4) | 0.222(3) | 0.294(5) | Fe | 0.500 | 0.0258(8) | 0.500 |

A slightly modified procedure was used for the synthesis of the following inclusion compounds. Complex **13** (1 mmol) was treated with β-cd (2.2 mmol) in water–ethylene glycol (1:1, 120 cm$^3$). The naphthalene complex **17** was dissolved in acetone (10 cm$^3$) at 50 °C and added to an aqueous solution of α- or β-cd in water (20 cm$^3$) at 50 °C. Complexes **18**, **22**, **27** and **28** were added as fine crystals to aqueous solutions of the cyclodextrins and stirred for several hours at 60 °C. Complex **26** (1 mmol) and γ-cd (2.2 mmol) were stirred for 8 h in water (100 cm$^3$) at 90 °C. The resulting orange suspensions were filtered at room temperature and the residual solids washed and dried as described above. Analytical data for the new inclusion compounds are summarised in Table 6.

*Crystal Structure Analyses.*—The crystals were obtained as yellow, transparent prisms. A Philips PW1100 automatic diffractometer was used for data collection. Cell constants are given in Tables 3–5 and details of data collections and structure refinements are summarised in Table 7. The reflections intensities were corrected for Lorentz and polarisation effects. The structures were solved using the program system DIRDIF.[21] The positions of the atoms of one cd molecule were submitted to the sub-program ORIENT. In subsequent Fourier difference maps all non-hydrogen atoms of the adducts of complexes **19** and **15** could be located. In the structures of the α-cd adducts of **4**, **6**, **9**, **29** and the β-cd adducts of **12** and **14** the guest complexes are highly disordered and many electron-density peaks could be observed in the cavities of the cyclodextrin dimers. The two structures of the β-cd inclusion compounds are isomorphous. The intensities of the adduct of **14** of parity ($h + k =$ odd) were very weak, those of the adduct of **12** could not be observed at all, thus leading to space group *C*2 in the latter case. Because of the disorder no further attempt was made to refine the parameters of the adduct of **14**. In the structure of the adduct of **12** the highest peak in the cavity was assigned to the iron atom. A similar case of isomorphism was reported for 2β-cd•$KI_7$•$9H_2O$.[22] Because of the limited number of observed reflections in all structures all atoms were refined isotropically using full-matrix least-squares methods. The applied weighting scheme was $1/\sigma(F_o)$. Attempts to refine them anisotropically resulted in unrealistic thermal parameters. The atomic scattering factors were taken from ref. 23. Final atomic co-ordinates of the α-cd adducts of **19** and **15** are listed in Tables 8 and 9, selected bond lengths and angles in Tables 10 and 11. The fractional atomic coordinates of **12**•2β-cd are given in Table 12. In addition to the programs cited, SDP[24] and SCHAKAL[25] were used.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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