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Coordination Chemistry Reviews
185–186 (1999) 601–617

COORDINATION
CHEMISTRY
REVIEWS

Structural chemistry of supramolecular assemblies that place flat molecular surfaces around the curved exteriors of fullerenes

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Contents

Abstract

An overview of the structural chemistry of fullerene compounds that are at least partially encapsulated by other moieties, (aromatic rings, calixarenes, metalloporphyrins) or ions (silver nitrate), is given.

Keywords: Fullerene compounds; Supramolecular assemblies; Flat molecular surfaces

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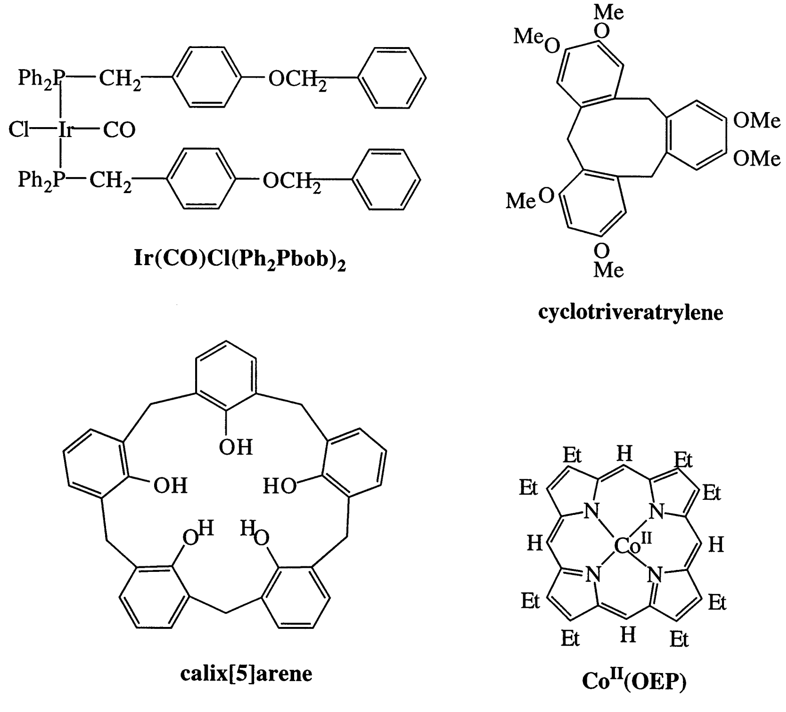
PII: S0010-8545(99)00013-2

1. Introduction

In recent reviews, four major types of reactions of fullerenes with transition metal complexes were identified [1,2]. These reactions include: (1) addition of a metal center to an olefinic C–C bond at a fullerene 6:6 ring junction to form η^2-coordination complexes, (2) reduction of the fullerene to form fulleride salts, (3) addition of a ligating group within the metal complex to the fullerene so that the metal center is attached to the fullerene through a bridging group, and (4) the formation of solids in which the fullerene and a metal complex are co-crystallized. Fullerenes have an interesting ability to co-crystallize with a variety of molecules that include organic (e.g. benzene [3]), organometallic (e.g. ferrocene [4]), as well as inorganic species (e.g. Pd_6Cl_{12} [5], P_4 [6], S_8 [7]). The three dimensional shapes of the fullerenes coupled with their distinct physical properties make them attractive candidates for the construction of larger, supramolecular arrays. The curved external surfaces of the fullerenes present interesting challenges in the design of larger assemblies. Here we give an overview of structural studies of compounds in which there is a significant, non-covalent interaction of the surfaces of a fullerene with other molecules, and in particular the flat surfaces presented by phenyl rings, collections of phenyl rings that are held together by additional bonding, porphyrins, and nitrate ion. The structural formulae of some of the compounds that are involved in these studies are shown in Scheme 1.

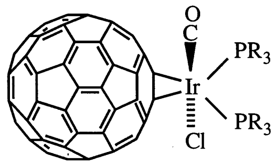


Scheme 1.

2. Tailoring ligands in iridium complexes to surround fullerenes

$Ir(CO)Cl(PPh_3)_2$ and related complexes with different phosphine ligands react with C_{60} and higher fullerenes through addition to a 6:6 ring junction as shown in Eq. 1, [1,2,8,9]. This straightforward adduct formation is generally a reversible process.

$C_{60} + Ir(CO)Cl(PR_3)_2 \rightleftharpoons$



(1)

The ease of dissociation and reassociation has a great advantage in that it facilitates the preparation of crystalline adducts that are suitable for single crystal X-ray diffraction [10]. The structures of the resulting adducts frequently show not only the η^2-coordination of the iridium to the fullerene but also secondary interactions in which aryl rings on the phosphine ligands undergo face-to-face interactions with the fullerene. For example, the structure of $(\eta^2\text{-}C_{70})\{Ir(CO)Cl(PhPMe_2)_2\}_2 \cdot 3C_6H_6$ is shown in part A of Fig. 1, [11]. In this double addition product, the two iridium complexes are bound at opposite ends of the fullerene, and all four phenyl rings of the two phosphine ligands make $\pi-\pi$ contact with the fullerene portion. The methyl substituents on the phosphine ligands are directed away from the fullerene. Additionally, one of the phenyl rings is sandwiched between two fullerene moieties as seen in the stereoscopic view of the solid state molecular packing (see part B of Fig. 1).

The presence of face-to-face fullerene/arene contacts in many crystalline fullerenes suggested that new phosphine ligands could be prepared to enhance such $\pi-\pi$ interactions. The new ligand, $Ph_2PCH_2C_6H_4OCH_2C_6H_5$ (Ph_2Pbob), was designed with flat aromatic portions which are connected in a flexible manner that allows them to clasp the curved exterior of a fullerene [12]. This ligand was readily converted into $Ir(CO)Cl(Ph_2Pbob)_2$, which reacts with C_{60} to form black crystals of $(\eta^2\text{-}C_{60})Ir(CO)Cl(Ph_2Pbob)_2$. The fullerene is bound to iridium in the expected η^2-fashion at a 6:6 ring junction. The two benzyloxybenzyl groups of one molecule of the complex cradle the C_{60} portion of the adjacent molecule. Fig. 2 shows three molecules embracing each other to form a portion of the linear array which extends throughout the crystal. The packing efficiency in this solid is remarkable. Two of the phenyl rings of each benzyloxybenzyl group make face-to-face π-contact with an adjacent fullerene, while another phenyl ring makes face-to-face contact with the fullerene within the molecule itself. The remaining phenyl ring of each phosphine ligand fits snugly between two columns of the complexes. While $Ir(CO)Cl(Ph_2Pbob)_2$ readily forms a crystalline solid with C_{60}, it does not react with C_{70} to yield crystalline material under similar conditions. The failure to crystallize such an adduct may result from the larger size of C_{70} and its inability to form the compact structure seen for the C_{60} adduct.

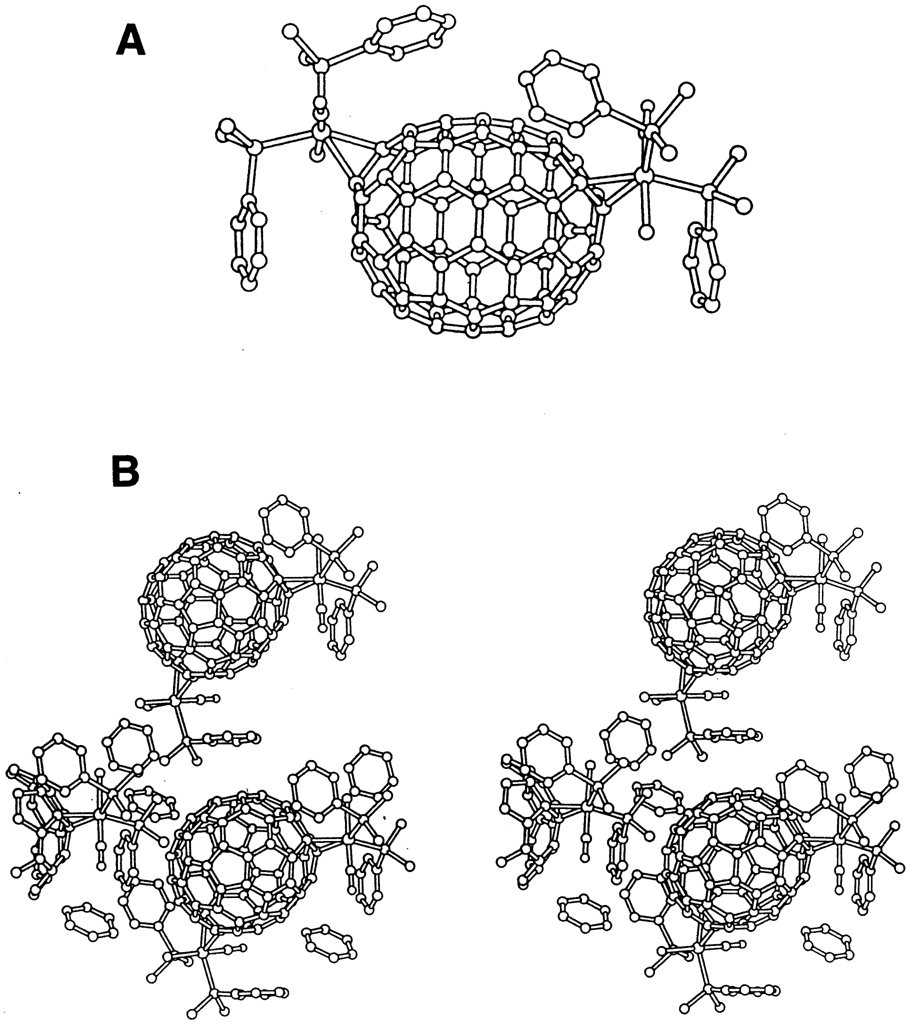


Fig. 1. (A) A view of the adduct $(C_{70})\{Ir(CO)Cl(PhPMe_2)_2\}_2$. (B) A portion of the solid state structure of $(C_{70})\{Ir(CO)Cl(PhPMe_2)_2\}_2 \cdot 3C_6H_6$ in which the C_{60}/phenyl interactions are emphasized. Taken with permission from the Ph.D. Thesis of J.W. Lee, University of California, Davis, CA, USA, 1994. See also A.L. Balch, J.W. Lee, M.M. Olmstead, Angew. Chem. Int. Ed. Engl. 31 (1992) 1356.

Related dendrimeric ligands, Ph_2P(3,5-bis(benzyloxy)benzyl) (PPh_2(G-1)) and Ph_2P(3,5-bis(3,5-bis(benzyloxy)oxybenzyl) (PPh_2(G-2)), which incorporate five and nine benzene rings into each phosphine, have been prepared [13]. They have been incorporated into iridium complexes and used to study the thermodynamics of the reversible binding of C_{60} to $Ir(CO)Cl(PPh_2G\text{-}1)_2$ and $Ir(CO)Cl(PPh_2G\text{-}2)_2$. In chlorobenzene solution, the dendrimeric arms of the phosphine ligands do not play a major role in stabilization of the fullerene adducts. Unfortunately, solubility

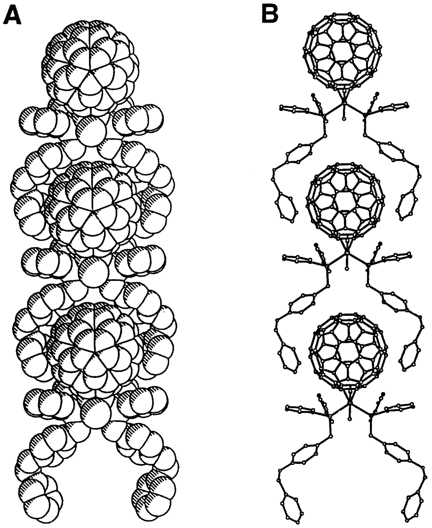


Fig. 2. Two views of the interaction of three molecules of $(\eta^2\text{-}C_{60})Ir(CO)Cl(Ph_2Pbob)_2$ in the solid state; (A) shows the van der Waals contours, while (B) shows the bonding framework. Notice how four of the aromatic rings of the Ph_2Pbob ligands cup the curved surface of the fullerene. Crystallographic data are taken from A.L. Balch, V.J. Catalano, J.W. Lee, M.M. Olmstead, J. Am. Chem. Soc. 114 (1992) 5455.

considerations preclude examination of the behavior in non-aromatic solvents where these ligands might have a larger effect on the stability of the adducts.

3. Preorganized arrays of aromatic rings: calixarenes, cyclotriveratrylene

Calixarenes and cyclotriveratrylene are organic molecules (see Scheme 1) with preorganized shapes which allows them to effectively interact with the fullerenes to form ball and socket structures. Additional donor–acceptor interactions, with the bowl-shaped arenes acting as donors and the fullerenes as acceptors, are likely to play a significant role in facilitating adduct formation. Selective complexation of crude fullerene soot with *p*-*t*-Bu-calix[8]arene followed by a series of recrystallizations has been utilized to purify C_{60} [14]. Several structural studies have been conducted that allow the ball and socket structures of the resulting aggregates to be visualized.

Treatment of C_{60} with trimethyl-, diiodo-calix[5]arene yields purple crystals of $C_{60} \cdot 2$(trimethyl-, diiodo-calix[5]arene) [15]. The structure of the aggregate is shown in Fig. 3. The C_{60} molecule is surrounded by two calixarene molecules that sit at opposite sides of the fullerene.

Addition of cyclotriveratrylene to a solution of C_{60} in toluene produces black crystals with the composition, $1.5C_{60} \cdot$(cyclotriveratrylene)$\cdot$(toluene) [16]. The X-ray crystal structure reveals that a one-to-one adduct is present as shown in Fig. 4. Additionally there is a disordered fullerene at a site of 2/m symmetry and a highly

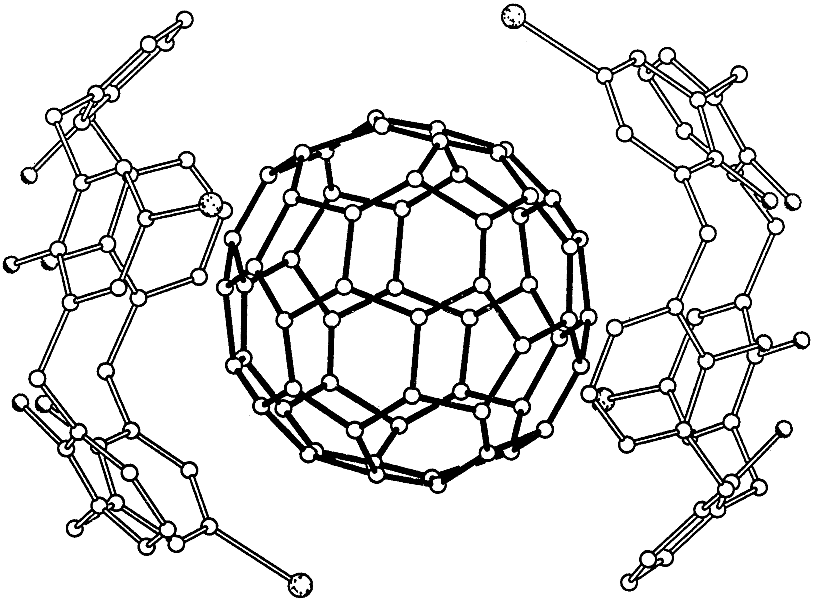


Fig. 3. A drawing of the cupping of C_{60} by two molecules of calix[5]arene in crystalline $(C_{60})\cdot$(calix[5]arene)$\cdot 8H_20$. Crystallographic data are taken from T. Haino, M. Yanase, Y. Fukazawa, Angew. Chem. Int. Ed. Engl. 36 (1997) 259.

disordered toluene molecule in the solid. Within the ball and socket structure shown in Fig. 4 however, the fullerene is ordered. One 3-fold axis of the C_{60} molecule is coincident with the 3-fold axis of the cyclotriveratrylene molecule. The separation between the carbon atoms of the fullerene and those of the cyclotriveratrylene is 3.51 Å, and the separation between the carbon atoms of the fullerene and the oxygen atoms of the cyclotriveratrylene is 3.34 Å.

Evaporation of solutions of C_{60} or C_{70} in the presence of calix[6]arene yields crystals of $2C_{60}\cdot$(calix[6]arene) or $2C_{70}\cdot$(calix[6]arene), respectively [17]. These crystals have been studied by X-ray diffraction. The original analysis focused on the two fullerene molecules nested within the shallow cavities of the calixarene [18,19]. However, further examination of the crystallographic data shows that the calixarenes actually make contact with fullerenes on both sides. Thus, each calixarene in this solid is nestled within a tetrahedral hole formed between four C_{60} molecules. Two views of the resulting structure are shown in Fig. 5.

Not all calixarenes can form a ball and socket structure about a fullerene core. Calix[4]arenes have too small a cavity to participate in the ball and socket arrangements. Although *p*-bromocalix[4]arene propyl ether co-crystallizes with C_{60}, the product consists of separate columns of C_{60} molecules and *p*-bromocalix[4]arene propyl ether molecules [19].

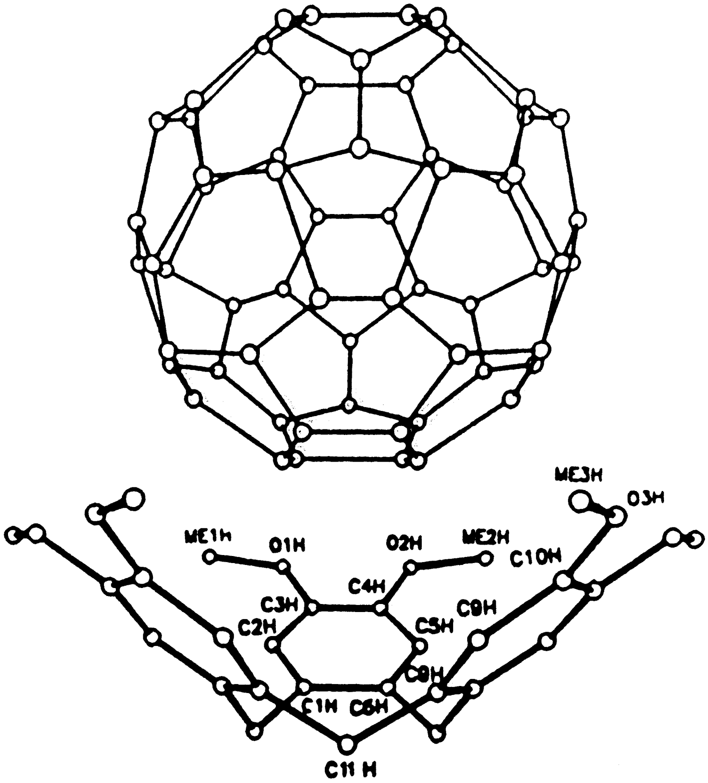


Fig. 4. A view of the ball and socket arrangement of a cyclotriveratrylene molecule and a C_{60} molecule in crystalline $1.5(C_{60})\cdot$(cyclotriveratrylene)$\cdot$0.5(toluene). Reproduced from J.W. Steed, P.C. Junk, J.L. Atwood, M.J. Barnes, C.L. Raston, R.S. Burkhalter, J. Am. Chem. Soc. 116 (1994) 10346.

4. Larger flat surfaces: metalloporphyrins

Mixing a benzene solution of C_{60} and a chloroform solution of $Co^{II}(OEP)$ or $Zn^{II}(OEP)$ produces crystals of $C_{60}\cdot 2Co^{II}(OEP)\cdot CHCl_3$ or $C_{60}\cdot 2Zn^{II}(OEP)\cdot CHCl_3$, respectively. The structures of the two compounds are isomorphic and contain an ordered C_{60} cage surrounded by two $M^{II}(OEP)$ units. A view of the $C_{60}\cdot 2Co^{II}(OEP)$ array is shown in Fig. 6. The fullerene is positioned asymmetrically between the two $Co^{II}(OEP)$ units, but it is too far from the cobalt atoms for any covalent bonding. The closest approach of the fullerene to the cobalt atoms involves 6:6 ring junctions. The distances from the cobalt atoms to the midpoints of these C–C bonds are 2.68 and 2.89 Å, respectively. The relevant Co–C distances are: 2.738, 3.198, 2.858, and 2.673 Å, whereas a covalent Co–C bond would have a shorter length of ca. 2.0 Å. While these distances are too long to represent coordination, they are shorter than normal van der Waals contacts which would be expected to produce separations between the porphyrin and the fullerene in the 3.3–3.5 Å range. It is likely that there is a degree of charge transfer

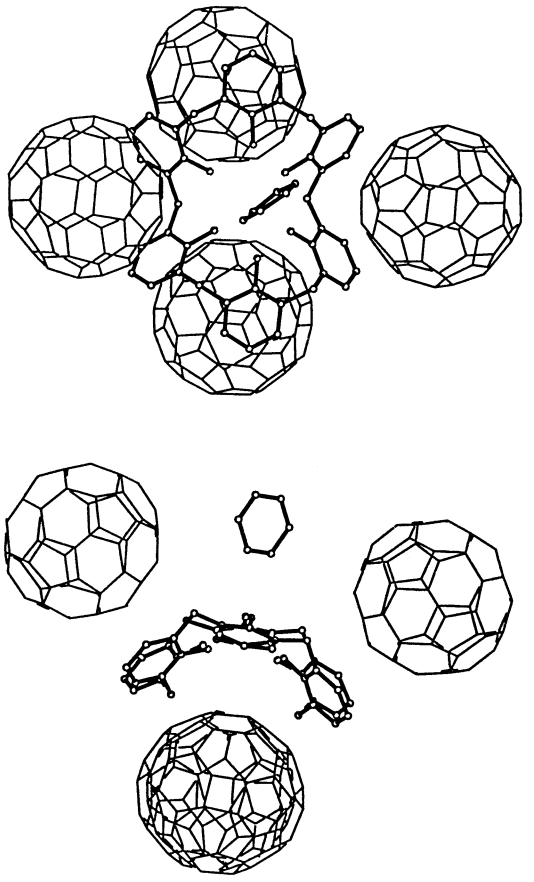


Fig. 5. Two views of the arrangement of four fullerenes about a calix[6]arene molecule in crystalline $2C_{60} \cdot$ (calix[6]arene). Crystallographic data are taken from J.L. Atwood, L.J. Barbour, C.L. Raston, I.B.N. Sudria, Angew. Chem. Int. Ed. 37 (1998) 981.

between the metalloporphyrin and the fullerene with the metalloporphyrin acting as a donor and the fullerene acting as an acceptor.

In addition to the close approach of the fullerene to the porphyrin plane, these crystals display two other features that are characteristic. (1) All eight of the ethyl groups are arrayed so that they grasp the fullerene in an octopus-like fashion. (2) The M^{II}(OEP) units are aligned in close face-to-face proximity. Fig. 7 shows how the $C_{60} \cdot 2Co^{II}$(OEP) units form extended helical ribbons thorough face-to-face contact between the porphyrins. The porphyrin–porphyrin overlap is more extensive in these co-crystalline materials than that seen in the pure, crystalline metalloporphyrins themselves [20,21].

Crystals of $C_{70} \cdot Co^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$, $C_{70} \cdot Ni(OEP) \cdot C_6H_6 \cdot CHCl_3$, and $C_{70} \cdot Cu(OEP) \cdot C_6H_6 \cdot CHCl_3$ are similarly formed from solutions of the fullerene

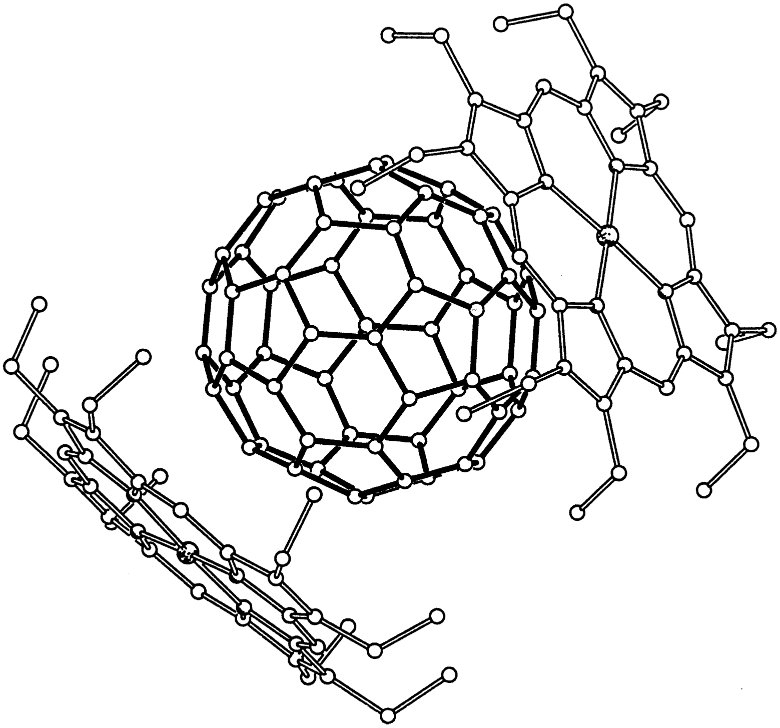


Fig. 6. A view of $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$ that shows how the two porphyrins surround the fullerene. Crystallographic data are taken from M.M. Olmstead, D.A. Costa, K. Maitra, B.C. Noll, S.L. Phillips, A.L. Balch, submitted for publication.

and the metalloporphyrin [22]. In these three isomorphic crystals, there is only one porphyrin/fullerene contact. A view of the spatial organization of the fullerene and the porphyrin is shown in Fig. 8. As in the case of the C_{60} compound shown in Fig. 6, there is no covalent bonding between the metal atom and the C_{70} molecule. The

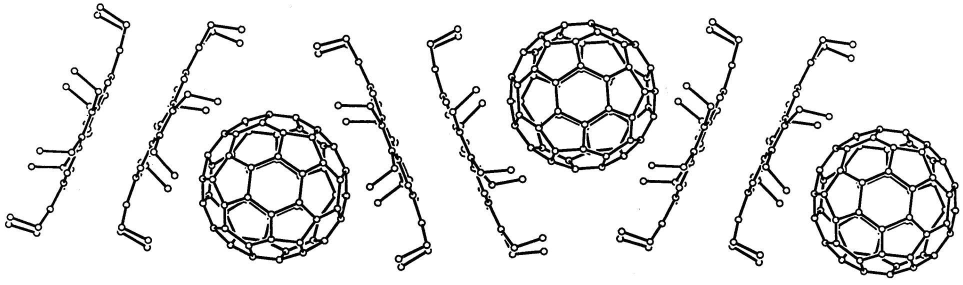


Fig. 7. A view of a ribbon of $C_{60} \cdot 2Co^{II}(OEP)$ molecules in $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$. Crystallographic data are taken from M.M. Olmstead, D.A. Costa, K. Maitra, B.C. Noll, S.L. Phillips, A.L. Balch, submitted for publication.

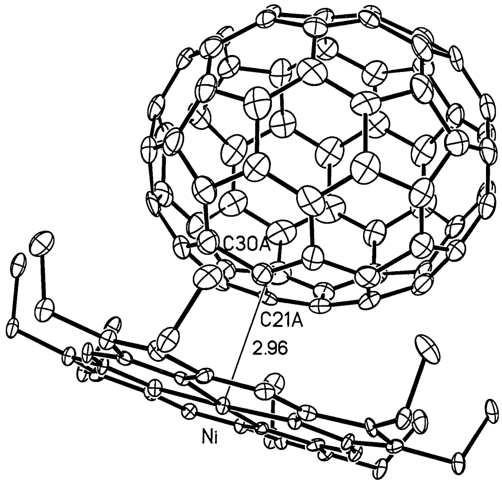


Fig. 8. A drawing of a portion of the structure of $C_{70} \cdot Ni(OEP) \cdot C_6H_6 \cdot CHCl_3$. Crystallographic data are taken from M.M. Olmstead, D.A. Costa, K. Maitra, B.C. Noll, S.L. Phillips, A.L. Balch, submitted for publication.

fullerene is positioned so that one of the carbon atoms (an atom in layer c of the fullerene) is positioned almost directly over the metal at the center of the porphyrin. For the cobalt complex the short, non-bonded Co···C distance is 2.800 Å. The fullerene is oriented so that the C_5 axis of the fullerene makes an angle of 16.4° with the porphyrin plane.

In $C_{70} \cdot Co^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$ there is close, face-to-face contact between the porphyrin planes, which involves a plane-to-plane separation (3.18 Å) and a lateral displacement of the two metal atoms that are similar to those seen in $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$. Again the ethyl groups are all arranged so that they both embrace the fullerene and avoid contact with the adjacent $Co^{II}(OEP)$ molecule.

Since the fullerene cages are ordered in the co-crystalline compounds described in this section, it is anticipated that co-crystallization of metalloporphyrins may offer a convenient method of obtaining suitable crystals of related compounds, i.e. endohedral metallofullerenes, higher fullerenes and chemically modified fullerenes, for study by single crystal X-ray diffraction. Additionally, the interactions between porphyrins and fullerenes (seen in Figs. 6–8) also serve as models for the interactions involved in the chromatographic separations of fullerenes on supports which bear appended porphyrins [23]. Other cases where fullerenes and related large, flat molecules are found in close proximity include: $C_{60} \cdot$ 2(octakis(dimethylamino)-porphyrazine) · (toluene) [24], a pyrrolidine-linked tetraphenylporphyrin/C_{60} dyad [25], and a variety of metal-free tetra-(substituted-aryl)porphyrins [26].

5. Encapsulation by independent molecules: hydroquinone

Mixing C_{60} or C_{70} with hydroquinone in benzene solution results in the precipitation of crystals of either $C_{60} \cdot 3$(hydroquinone) or $C_{70} \cdot 4.5$(hydroquinone) · (benzene) [27,28]. These solids consist of a framework of hydroquinone molecules which form large cages that encapsulate the fullerenes. The hydroquinone molecules self-associate through an extensive network of H–O···H hydrogen bonds. Fig. 9 presents a stereoview of a portion of the structure of $C_{60} \cdot 3$(hydroquinone) that was selected to show one cage. Within the cage the fullerene is extensively disordered. Notice the bowl-shaped moieties at the top and bottom of the cage where three hydroquinone molecules surround the fullerene in face-to-face fashion. These three hydroquinone molecules are in turn hydrogen-bonded with three others (which are not shown in their entirety). The ends of these six hydroquinone molecules form $(OH)_6$ rings with the oxygen atoms in a chair conformation. In addition to the six hydroquinone molecules that make face-to-face contact with the fullerene, there are an additional six hydroquinone molecules that make edge-to-face contact with the C_{60} molecule.

The solid state architecture of $C_{70} \cdot 4.5$(hydroquinone) · (benzene) involves similar cages. Bowl-shaped moieties are again present in which three hydroquinone molecules surround cavities in face-to-face fashion. These three hydroquinone molecules are hydrogen-bonded with three others to form $(OH)_6$ rings with the oxygen atoms in a chair conformation. However, unlike the case in $C_{60} \cdot 3$(hydroquinone) where all of the cages are the same, in $C_{70} \cdot 4.5$(hydroquinone) · (benzene) there are three different types of cages: a peanut cage that encloses two C_{70} molecules, a second cage that encloses just a single C_{70} molecule, and a third cage that encapsulates two benzene molecules.

6. Encapsulation by an ionic compound: silver nitrate

Dark red, nearly black blocks of $C_{60} \cdot 5\{Ag(NO_3)\}$ are prepared by the diffusion of a solution of silver nitrate in ethanol into a solution of C_{60} in benzene [29]. A

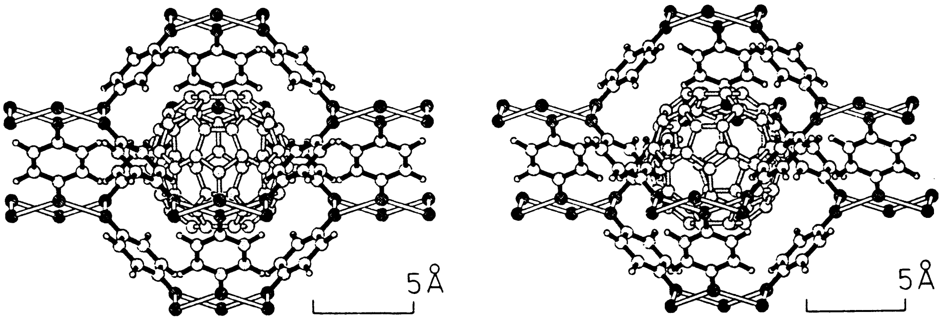


Fig. 9. A stereoscopic drawing that shows the encapsulation of C_{60} by hydroquinone molecules in crystalline $C_{60} \cdot 3$(hydroquinone). Reproduced from O. Ermer, Helv. Chim. Acta 74 (1991) 1339.

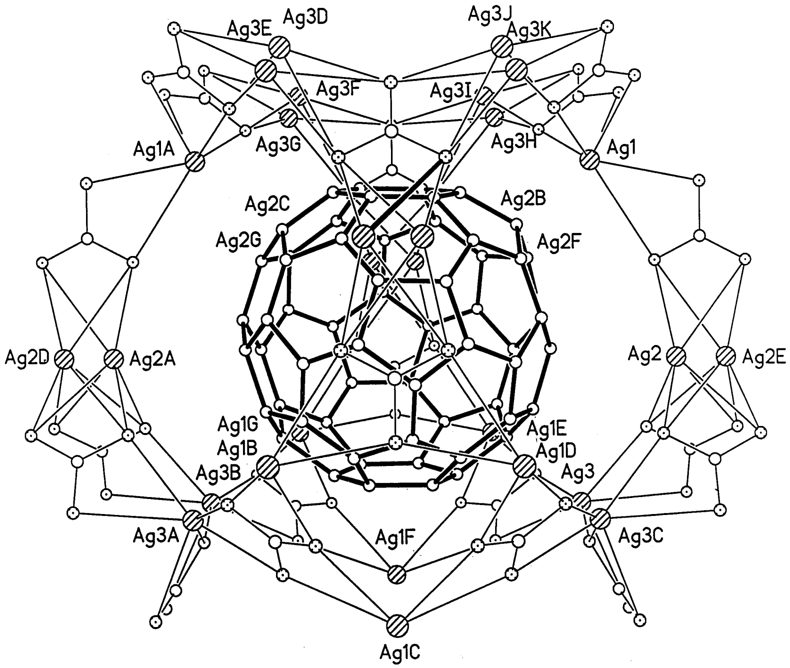


Fig. 10. A view of a portion of the structure of crystalline of $C_{60} \cdot 5\{Ag(NO_3)\}$ that shows how the extended silver nitrate network encapsulates one fullerene. Only one orientation of the fullerene is shown. Hatched circles are the silver ions, open circles are the nitrogen atoms, and the circles with a dot at the center are the oxygen atoms. Crystallographic data are taken from M.M. Olmstead, K. Maitra, A.L. Balch, Angew. Chem. Int. Ed. Engl. 38 (1999) 231.

view of the structure is shown in Fig. 10. The solid consists of an extended network of silver nitrate ions in which each silver ion is in contact with six oxygen atoms from the nitrate ions. The Ag–O distances range from 2.34(12) to 2.814(12) Å. This silver nitrate network forms zeolite-like cages that encapsulate the C_{60} molecules. (In other studies C_{60} has been introduced into the cavities in a preformed, large pore aluminophosphate [30]). However, the silver nitrate network encapsulates each fullerene in a fashion that precludes movement of the fullerene molecules from one cavity to another. There are four 'straps' which surround the fullerene in two perpendicular planes. Fig. 11 shows some details of the arrangement of two of the straps, the ones that come closest to the C_{60} molecule. One of the silver ions, Ag1, is situated on a mirror plane perpendicular to **a** (position *m*). A second silver ion, Ag2, also resides on this plane but is disordered with respect to the mirror plane that is perpendicular to **b** (position *d*). The Ag2···Ag2′ distance is 1.137(9) Å. The third silver ion, Ag3, is disordered about a center of inversion (position *e*) and is separated from its centrosymmetric counterpart by 0.633(13) Å. The C_{60} molecule resides at a site (position *d*) with mm symmetry.

The fullerene cavity is located at the intersection of two perpendicular mirror planes. However, the fullerene molecules are not centered within this site. Rather, the center of the C_{60} molecule is shifted 0.185 Å from the special position of mm symmetry, and one of the fullerene mirror planes is rotated by 5.2° from the crystallographic mirror plane. Thus, there are four possible locations for the fullerene within a cavity. Fig. 11 shows one of those orientations and the nature of the fullerene–silver contacts along the straps that interact most closely with the fullerene. The other two straps are positioned further away from the fullerene. The contacts between Ag2 and Ag3 and the fullerene carbon atoms are quite long and do not correspond to normal bonding distances. However, Ag1 does interact with the fullerene in two ways. On one side it engages in η^2-coordination with Ag–C distances (2.590(10) and 2.698(10) Å) that are within the range found for such bonding. On the opposite side, the Ag1–C1 distance, 2.213(6) Å, is quite short and the location of the silver ion is directly over a single carbon atom so that η^1-coordination is involved. This is the first case of η^1-coordination of a transition metal to a fullerene that is crystallographically determined [1]. (The fullerene was modeled as a rigid group. Consequently, distortion of the fullerene by coordination is masked, and the Ag–C distances are subject to additional uncertainties.) It is known that silver ions can interact with olefins and aromatic hydrocarbons in both η^1- and η^2- fashion [31]. Moreover, the silver ion is not necessarily symmetrically disposed with respect to the olefin in cases of η^2-bonding.

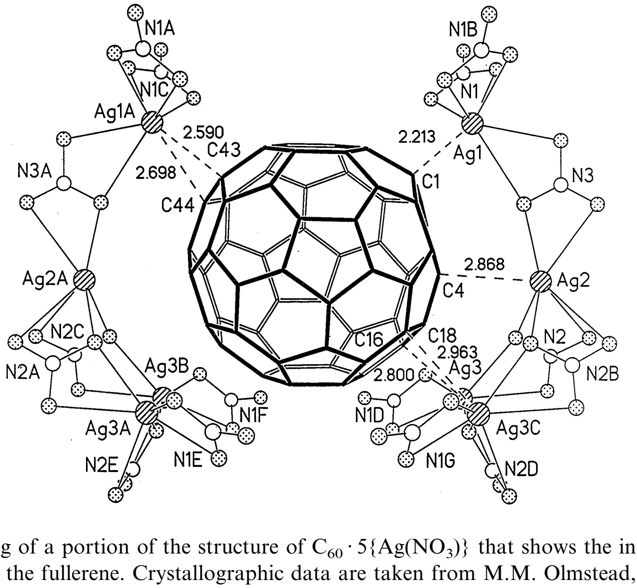


Fig. 11. A drawing of a portion of the structure of $C_{60} \cdot 5\{Ag(NO_3)\}$ that shows the interactions of two of the straps with the fullerene. Crystallographic data are taken from M.M. Olmstead, K. Maitra, A.L. Balch, Angew. Chem. Int. Ed. Engl. 39 (1999) 231.

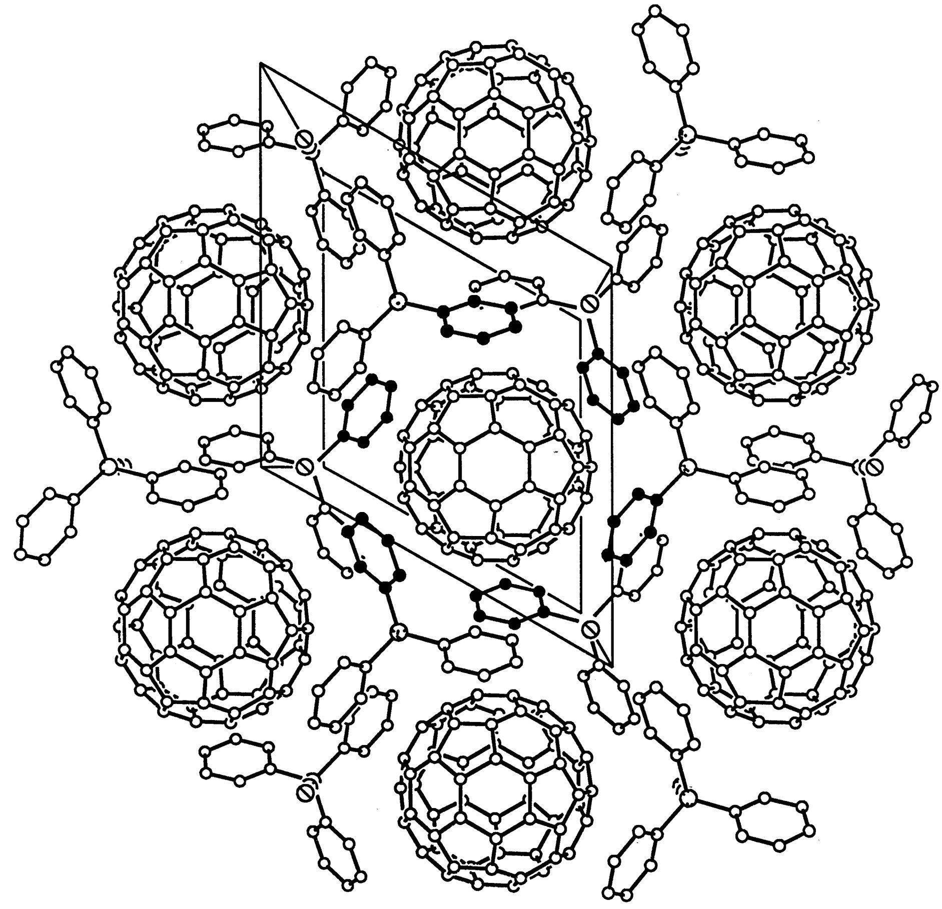


Fig. 12. A drawing of the structure of $C_{60} \cdot 2(Ph_3As)AuCl$ that shows the six phenyl rings (with carbon atoms shown as solid circles) that surround each fullerene in the layer. Crystallographic data are taken from M.M. Olmstead, K. Maitra, A.L. Balch, unpublished results.

7. Encapsulation through co-crystallization with $(Ph_3As)AuCl$

Black crystals of $C_{60} \cdot 2(Ph_3As)AuCl$ precipitate from a benzene solution of the two components. The structure of the resulting solid, as determined by a single crystal X-ray diffraction study, is shown in Fig. 12, [32]. The molecules pack so that there are six phenyl rings from six different $(Ph_3As)AuCl$ molecules that make face-to-face contact with the fullerene as seen in Fig. 12. These contacts are organized so that layers exist in the solid in which each fullerene in the layer is surrounded by these arrays of six phenyl rings. In the next layer of the solid the Au–Cl portion of the $(Ph_3As)AuCl$ complexes sits over the fullerenes and there are no ball-to-ball contacts. The three phenyl rings of each $(Ph_3As)AuCl$ molecule makes face-to-face contact with three different C_{60} molecules. Fig. 13 shows the

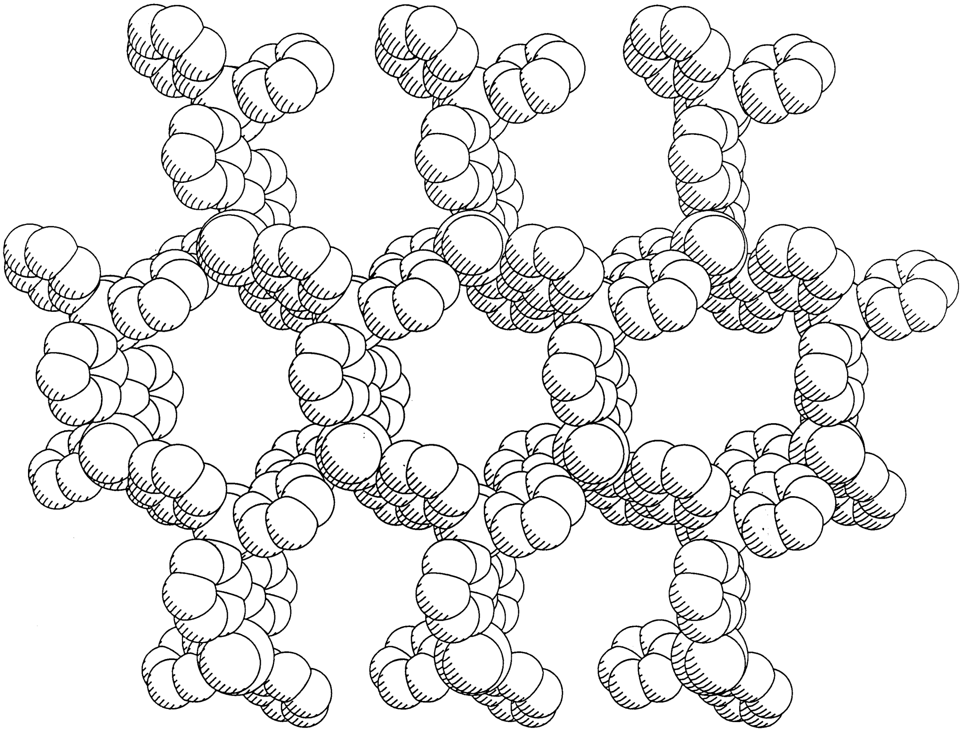


Fig. 13. A view of the structure of $C_{60} \cdot 2(Ph_3As)AuCl$ with the fullerene molecules removed. The circular cavities where the fullerenes reside are clearly apparent. Crystallographic data are taken from M.M. Olmstead, K. Maitra, A.L. Balch, unpublished results.

network of molecules in $C_{60} \cdot 2(Ph_3As)AuCl$ with the fullerene molecules removed. The round cavities into which the fullerene molecules fit are clearly visible.

8. Conclusions

A number of complex aggregates can be formed about fullerene templates. With organic molecules such as the calixarenes and cyclotriveratrylene, the host structures are already organized into bowl-shaped units that have the proper dimensions to surround a portion of the fullerene surface. In other cases such as the ligands in $Ir(CO)Cl(Ph_2Pbob)_2$ and $C_{60} \cdot (Ph_3As)AuCl$ and with hydroquinone independent but flexible, units are seen to adopt orientations that conform to the fullerene surface. Even an ionic material, silver nitrate, has been found to form a network in which round, C_{60}-containing cavities are formed.

Acknowledgements

The authors thank the National Science Foundation (Grant CHE-9610507) for support and all of our co-workers, who are listed in the references, for their important contributions.

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