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Structural Diversity of Host–Guest and Intercalation Complexes of Fullerene C_{60}

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Pristine fullerene C_{60} has a *fcc* structure. Crystallisation of the fullerene in a variety of solvents can lead to inclusion complexes, as well as discrete host–guest complexes in the presence of cavitands and porphyrins, and related molecules. The complexes retain varying degrees of fullerene···fullerene interactions at the van der Waals limit, except in a limited number of cases where the fullerenes are completely shrouded by one or more included/host molecule. Analysis of the fullerene···fullerene interactions in these complexes reveals a diverse structural arrangement of the fullerenes. They can be organised into dimers, single linear columns or zigzag chains, double columns, spectacular fivefold Z-shaped columnar arrays, hexagonal close-packed layers, corrugated sheets, honeycomb motifs, non-close-packed layers and complex three-dimensional networks. Disorder of the fullerenes in the solid state is common, although structures with close-packed planar arrangements of C_{60} molecules and/or with symmetry matching between the host molecule and the fullerene (two-, three- and fivefold symmetry) tend to have less disorder of the fullerene.

Introduction

Icosahedral fullerene C_{60} readily forms intercalation complexes affording materials that contain small molecules such as haloforms[1,2] through to larger molecules like ferrocene,[3] curved- or bowl-shaped receptor molecules including modified calixarenes,[4] cyclotriveratrylene and related molecules,[5] porphyrins and metal macrocycles.[6] Some of these complexes have the fullerene completely shrouded by other molecules whereby the structures are devoid of fullerene···fullerene interactions, although most of them have fullerene···fullerene interactions to varying degrees. Herein, we analyse the structures of these complexes that were previously established using X-ray diffraction techniques, focusing on the nature of the fullerene···fullerene interactions (closest contacts), on any geometrical alignment of the polyhedral faces from adjacent fullerenes and on any disorder of the fullerenes. Such aspects of the structures are often overlooked or oversimplified despite their fundamental importance in developing the supramolecular chemistry of C_{60} and, ultimately, in devising ways of controlling the interplay of C_{60} molecules as a paradigm in crystal engineering in building up new materials with novel function. Indeed, the supramolecular chemistry of fullerenes has been used to control the interplay of fullerenes in the solid state, and fullerenes have been covalently linked under high pressure and temperature[7] and advances have been made in the building up of arrays of C_{60} that involve complexation with calix[5]arene.[8] Typically, the structure determination of fullerene complexes is carried out at ca. 150 K with no distinction between dynamic or static disorder.

General aspects of the supramolecular chemistry of fullerenes feature in various review articles;[9] these reviews include aspects of chemically modified C_{60}, which is beyond the scope of this review, although it is noteworthy that there have been some spectacular findings. The organization of the potassium salt of a pentasubstituted fullerene into ≈17-nm spherical bilayer vesicles,[10] the assembling of fullerenes on surfaces,[11] the binding of porphyrins[12] and assembling of 64 C_{60}^- anions on the surface a dendrimer with terminal ferricinium moieties[13] are particular noteworthy. Dendrimers can also bind fullerenes within their internal cavities;[14] these include porphyrin-containing systems.[15] In addition, self-assembly processes can stabilise nanoparticles of fullerenes, such as a diblock polymer shrouding, which involves approximately 10^{10} fullerene molecules.[16] Fuller-

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enes can also be taken up in the pores of mesoporous silica, with aggregation of the fullerenes in the presence of cavitand molecules. This process is the basis of a qualitative test for host–guest chemistry between the fullerene and cavitands in solution,[17] and confinement of the fullerene can be used to form hydrated C_{60} at 350 °C, i.e. by controlling the synthesis in a confined space.[18] Fullerenes, including metallofullerenes such as $Sm@C_{82}$,[19] and $C_{60}O$ can also be drawn inside carbon nanotubes.

The formation of inclusion complexes of C_{60} with small molecules such as solvent molecules has limited scope in building up new arrays since the relatively large fullerene molecules can still interact with several fullerenes, and fullerene···fullerene interactions dominate the extended structure. Inclusion complexes involving larger molecules tend to have less fullerene···fullerene interactions because the molecules can cover a larger part of the surface of the fullerene. The limiting case is when the fullerene is completely shrouded by other molecules, and clearly the greater the attraction between other molecules and the electron deficient C_{60}, the less likelihood of multiple fullerene···fullerene interactions or any such interactions. Optimising the complementarity of curvature and size of C_{60} with host molecules such as bowl-shaped cavitands and saddle-shaped molecules has been used to good effect in forming assemblies of host–guest complexes as part of extended structures with fullerene···fullerene interactions, although the origins of such work relate to the use of cavitand molecules as a means of purifying the fullerene through host–guest/molecular-recognition chemistry.[4]

Matching the curvature of C_{60} with that of potential host molecules is not an essential strategy for forming complexes, since planar porphyrins readily form complexes in the solid state with spheroidal fullerenes, often with the structures possessing fullerene···fullerene interactions.[20] In addition, the choice of solvent can effect the formation of host–guest complexes, tipping the balance from complexation to complexation with aggregation of the fullerenes through to little or no complexation. Even the presence of C_{70} can affect the nature of the host–guest complex of C_{60} with a host molecule.[23] Figure 1 summarises the main types of "host" molecules that have been used for the for-

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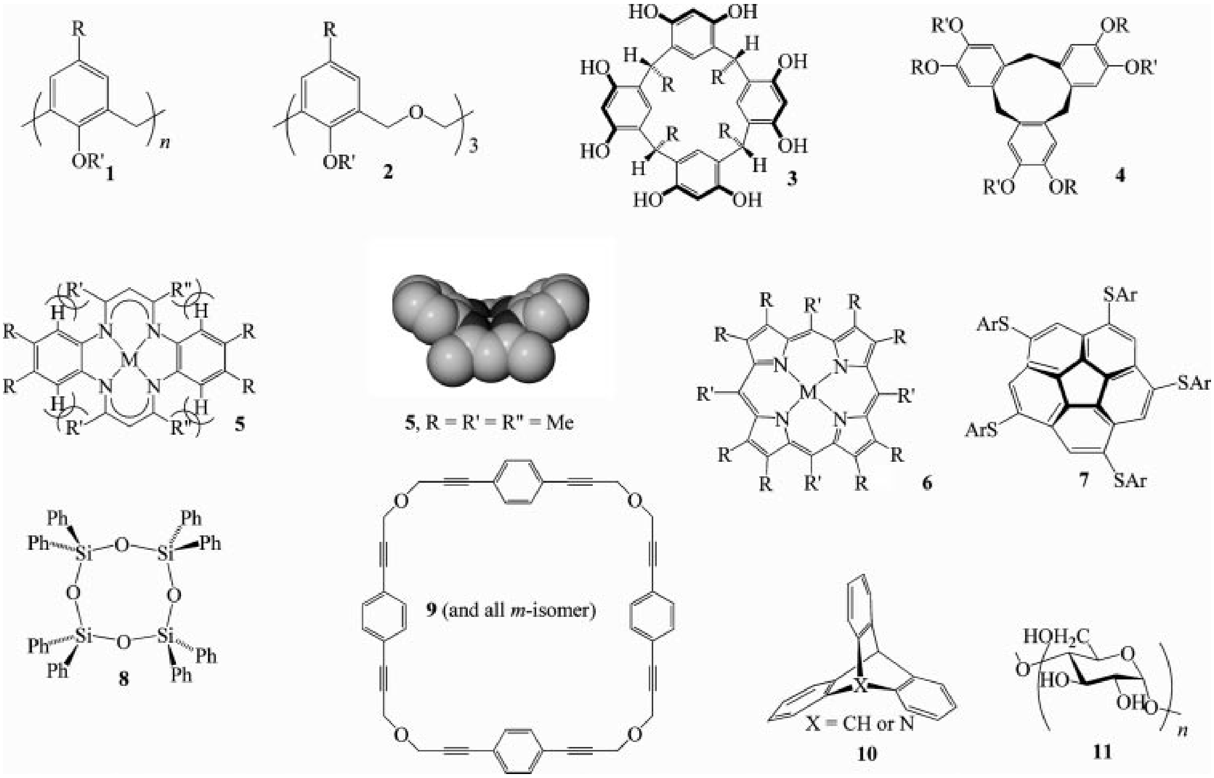


Figure 1. Types of molecules that form complexes with fullerenes with a specific example for **5** shown in space filling.

mation of complexes of C_{60} and includes cavitands **1**–**4**, **7**[21] and **9**,[22] saddle-shaped molecules **5**, porphyrins **6**, siloxanes **8**, curved-faced tryptophanes **10**,[23] and β- and γ-cyclodextrins (n = 7, 8) **11**, although not all of these lead to crystalline material and structure authentication by using diffraction data. When complexation is not prevalent, the addition of other synthons can be effective. For example, group 1 ions bind to modified calixarenes (R′ = ester), resulting in the complexation of C_{60}.[24] Seemingly, most molecules with aromatic-ring systems and electron-rich moieties can form complexes with C_{60}, including benzene and extended aromatic systems and tetrathiafulvalenes,[25] but the conditions to effect complexation can vary.

While the solid-state structures of many fullerene host–guest complexes of C_{60} have been determined, the focus of the structures has usually been on the nature of the host–guest interplay, often with little regard to the nature of the extended structure dealing with fullerene···fullerene interactions and to the nexus to the structure of *fcc* C_{60}. In analysing the extended structures, the indicator for fullerene···fullerene interactions is any centroid-to-centroid distance that is close to 10.0 Å (the van der Waals limit of

Table 1. Structural types for the arrangement of C_{60} molecules in the solid state.

Structural types	Number of examples	Number of structures with ordered C_{60}	Number of fullerenes with close contacts	Closest centroid···centroid fullerene distances [Å]
Pure C_{60}[26]	8	0	12	9.940
Encapsulated/Isolated fullerenes[27]	37	8	0	–
Dimers[28]	7	1	2	9.93–10.20
Single, linear columns[29]	6	1	2	9.90–10.10
Zigzag chains[30]	11	3	3	9.90–10.20
Double columns[31]	4	0	4	9.90–10.00
Fivefold Z-shaped columns[32]	1	0	4–6	9.90
Close-packed layers[33]	10	5	6	9.80–10.30
Nonclose-packed layers[34]	6	4	6	9.80–10.30
Corrugated sheets[35]	11	8	5	9.90–10.30
Honeycomb motif[36]	6	0	4	9.90–10.00
3D continuous networks[37]	23	10	4–6	9.90–10.20
Total[a]	126	40	60	

[a] Note that there are also twelve compounds in the appendix for which the structure is unknown because of lack of coordinate data or extreme disorder, and accordingly, are not included in the Table.

the fullerene). Fullerene C_{60} molecules can be positioned with different combinations of five- and six-membered rings facing each other, an edge facing a ring face, or two edges facing each other. The type of positioning affects the closest carbon-to-carbon distance – and to a certain extent the centroid···centroid distance. In general, for fullerene molecules at the van der Waals limit, the closest carbon-to-carbon distances are between 3.1–3.4 Å, depending on how the fullerene molecules are oriented. Thus, analysing different C_{60} arrangements also involves considering the state of order/disorder of the fullerenes. Table 1 summarises the salient information, including the number of compounds that exhibit a particular arrangement of C_{60} molecules, the proportion of each arrangement in which C_{60} is ordered and the proportion of each arrangement in which fullerene centroid···centroid distances are <10.30 Å. While this is slightly beyond the van der Waals limit, it nevertheless is a guide for the packing of the fullerenes in building up continuous structures.

The Extreme Cases – Pristine *fcc* and Encapsulated C_{60}

In pure *fcc* C_{60} (Figure 2), the centroid···centroid distance is 9.94 Å, and this is a reference point to compare centroid···centroid distances with complexes of the fullerene. Pure C_{60} contains disordered molecules, which is not surprising given the spheroidal nature of the fullerene in the absence of any directional contacts beyond the 12 fullerene···fullerene interactions for each fullerene.[26]

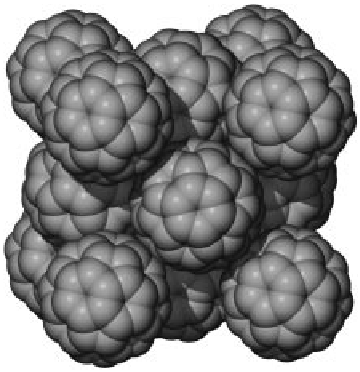
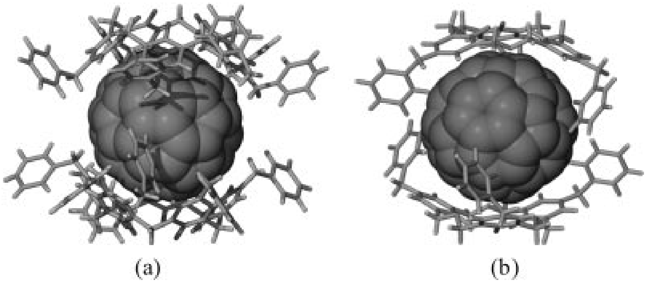


Figure 2. Space filling *fcc* for pristine C_{60}.[26]

In some complexes, each C_{60} molecule is completely encapsulated with no intimate contact with other C_{60} molecules, for example, in complexes of calix[5]arenes with *p*-substituted pendant arms (phenyl or benzyl) in which two calixarenes shroud each fullerene. For calix[5]arenes, the complementarity of size and shape of the fullerene with the cavity defined by the phenol moieties is striking. Calix[5]arene with H atoms in the *p*-positions can also form a complex in which two calixarenes interact with a central fullerene, but there is still enough room on the surface of the fullerene to allow close contacts with other fullerenes. This is part of a one-dimensional array of five columns of close-packed fullerenes in a Z-shaped array (see below).[8] This is a spectacular example of a simple change in substitution of calixarene that dramatically changes the nature of the complex.

p-Benzylcalix[5]arenes **1** form a 2:1 complex with C_{60} in which the fullerene is shrouded by two staggered *trans* host molecules in the cone conformation with dangling benzyl groups [Figure 3(a)].[38,39] Interestingly, the symmetry axis of the calixarene is aligned with a C_5 symmetry-element of C_{60}. However, in the case of the related C_{60} complex of *p*-phenylcalix[5]arene,[40] the rigid extended arms interdigitate in one hemisphere of the 2:1 supermolecule such that symmetry matching for both calixarenes is not possible, and the "confused" fullerene is now completely disordered.[40] Other authenticated structures in which C_{60} is encapsulated by two calix[5]arenes such that there are no interfullerene contacts include a calix[5]arene complex with three methyl and two iodo groups (1,3-disposition) in the *p*-positions of the upper rim.[41]



(a) (b)

Figure 3. Encapsulation of single fullerene C_{60}. Structure of (a) $[C_{60}\subset\{p\text{-benzylcalix[5]arene}\}_2]$ and (b) $[C_{60}\subset\{p\text{-benzyloxacalix[3]arene}\}_2]$.[38]

Oxacalix[3]arenes **2** also have complementarity of curvature with C_{60}, and *p*-benzyloxacalix[3]arene similarly forms a 2:1 complex in which two calixarenes shroud the fullerene. Here, a C_3 symmetry-axis of C_{60} lines up with the symmetry axis of the two host molecules in the *trans* arrangement, i.e. the fullerene is not disordered at the temperature at which the diffraction data were acquired, ca. 173 K.[38] The benzyl groups are edge-on to the fullerene, with C–H···fullerene interactions [Figure 3(b)], rather than face-on for π···π interactions, or the benzyl groups are directed away from the fullerene such as in the structure of the analogous *p*-benzylcalix[5]arene complex.[38] Clearly, symmetry matching is a worthwhile endeavour to afford ordered fullerene molecules in the solid state, at least at low temperature (ca. 173 K).

Dimeric Arrangement of C_{60} Molecules

In a few cases, C_{60} molecules are confined as pairs at the van der Waals limit (9.93–10.20 Å).[28] Only one compound has ordered fullerenes at the temperature of the X-ray diffraction studies. A striking feature of the 1:1 *p*-bromohomooxocalix[3]arene C_{60} complex is the relatively small

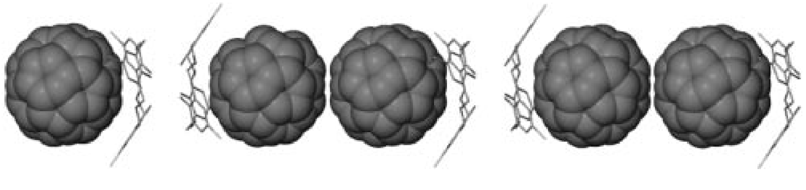


Figure 4. Inclusion complex C_{60} as van der Waals dimers sandwiched by two *p*-bromo-homooxocalix[3]arene molecules.[43]

calixarene that disrupts the interfullerene interactions. Isolated pairs of fullerenes have π···π interactions with the calixarenes, with distances between the centroids within the pairs of fullerenes of 9.93 Å. The cup shape of the calixarene and possible polarization effects from the bromine substituents presumably impact on the overall structure, which consists of the stacking of the dimeric columns as represented by the top view projection with no other fullerene···fullerene close contact other than that of the dimers, Figure 4.[43] While a trimeric aggregate of C_{60} molecules have been proposed for the structure of the 1:1 complex of C_{60} with *p*-*t*Bu-calix[8]arene,[42] its solid-state structure authentication remains elusive, and the same can be said of higher arrays. For the dimeric arrangement, there are only a couple of structures in which the fullerene molecules are ordered.

Single Linear Columns

A common arrangement of C_{60} molecules is as single linear columns with each fullerene in close contact to two fullerenes and the dihedral angle set at 180°. All structures have disordered fullerene molecules, and the fullerenes are at the van der Waals limit (10.1 Å) (Figure 5).[44]

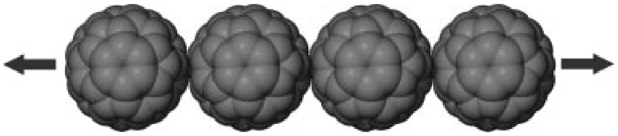


Figure 5. Single column arrays of C_{60} found in the structure of bis(1,3,5-triphenylbenzene)chlorobenzene clathrate; fullerene centroid-to-centroid distances: 10.10 Å.[44]

Zigzag Chains

C_{60} molecules can be organised into continuous zigzag chains, with varying C_{60}–C_{60} close contacts (9.90–10.20 Å). These chains are similar to linear columns, but with the C_{60} molecules offset with respect to each other and with the dihedral angle <180°. The dihedral angle ranges from 118 to 172° thus presenting the intermediate structures between linear-chains and double-column arrangements. There are more zigzag-chain structures than linear-column structures of C_{60}, and the proportion of ordered structures is much higher (Table 1). It is interesting that the zigzag chains (and corrugated sheets, see below) contain higher proportions of C_{60} centroid-to-centroid distances that are at the lower end of the van der Waals limits than linear columns and planar layers. This suggests that the zigzag arrangement of fullerenes encourages fullerene···fullerene interactions more than the linear counterparts.

The 1:1 complex between C_{60} and CTV (cyclotriveratrylene; **4**, R = R′ = Me), and the recent structure of the 1:1 complex of calix[5]arene and C_{60} (Figure 6), form zigzag structures. It is interesting to note that the CTV complex forms in toluene in the presence of a saturated solution of CTV (approximately 20-fold excess of CTV relative to the fullerene), whereas a fivefold excess of CTV gives a 3:2 complex that is rich in C_{60} and the fullerenes are arranged in close-packed, hexagonal sheets (see below).

Double Columns (Close Packed)

A few examples of C_{60} complexes crystallising with the fullerenes arranged into two close-packed columns have been authenticated. This is the limiting case for zigzag chains in which the dihedral angle between the fullerenes is 60° and each fullerene is in close contact with four other

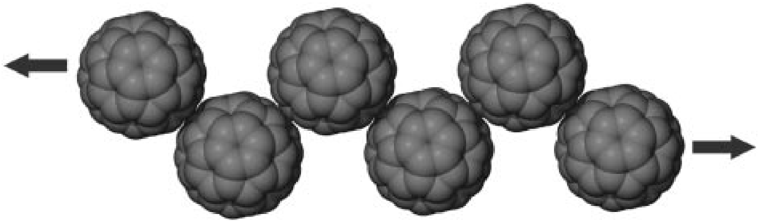


Figure 6. Zigzag fullerene arrangement in the structure of [C_{60}{calix[5]arene}]; fullerene centroid-to-centroid distances: 10.03 Å.[8]

fullerenes rather than with two (Figure 7). All of the complexes have some level of disorder, and the fullerene arrangement is depicted for the siloxane/C_{60}-fullerene complex in which each fullerene is surrounded by four others with centroid···centroid distances of 9.85–10.10 Å.[45]

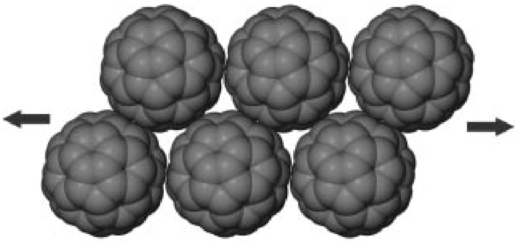


Figure 7. The double-columnar array in a siloxane/C_{60}-fullerene complex; centroid···centroid distances: 9.85–10.1 Å.[45]

Fivefold Z-Shaped Columns (Close Packed)

Calix[5]arene **1**, n = 5, R = R′ = H, forms a unique complicated complex with C_{60}, $[(C_{60})_5\{\text{calix[5]arene}\}_4]$,[32] in which the fullerenes assemble into five columns in a Z-arrangement [Figure 8(a)], which are surrounded by a sheath of calixarenes. The fullerenes are close packed in the columns with three different fullerene environments [Figure 8(b)]: (i) those on the outer columns, and each fullerene is in contact with four other fullerenes (cf. the environment the fullerene in the double-column arrangement, Figure 7), (ii) those in the two nearest columns of the bend of the "Z" shape, where the fullerenes have six close contacts, and (iii) the central column where each fullerene also has six close fullerenes, albeit now in a flat hexagonal arrangement. On the basis of analytical data, prior to the structure determination, the complex was thought to be a 1:1 complex rather than a 5:4 complex, and in this context, care needs to be exercised in establishing the stoichiometry of fullerene host–guest complexes in the absence of structural elucidation. Moreover, the presence of other fullerenes, and other globular molecules in solution, dramatically changes the nature of the complex that crystallises from solution. In the presence of C_{70}, which is the other major fullerene in fullerite, a 1:1 calixarene: C_{60} complex forms (see above).[8] Remarkably no C_{70} is incorporated into the structure, but it still predetermines the nature of the C_{60} complex formed. This is despite the solution binding constants that favour C_{70} complexation over that of C_{60}, and thus crystal packing forces must be more important. The same 1:1 complex involving C_{60} also forms in the presence of C_{84} and 1,2-dicarborane (1,2-$C_2B_{10}H_{12}$), an icosahedral molecule, which in the absence of C_{60} is drawn into the cavity of the calixarene.[46]

Close-Packed Layers

The structure of these 2D arrays takes on some aspects of the structure of *fcc* for pure C_{60}. Hexagonal close packing of the fullerene molecules occurs in several structures with fullerene···fullerene centroid-to-centroid distances of 10.0–10.2 Å (Figure 9). In comparison to other C_{60} arrangements, the proportion of structures in this category is relatively low, despite the fact that hexagonal close packing is a common arrangement for two-dimensional arrays of spheroidal moieties. Within these structures, the C_{60} molecules tend to be ordered, and in some cases, this relates to the interplay of the fullerenes with inclusion/host molecules on either side of the hexagonal arrays, as in the complex with CTV (see below).[47]

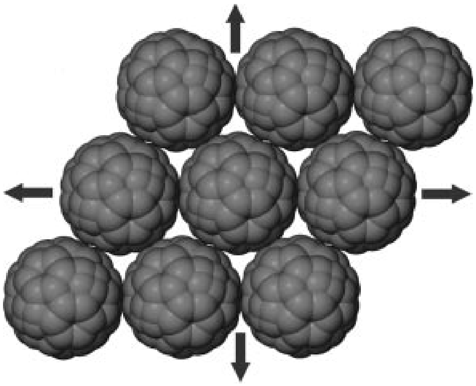


Figure 9. Hexagonal close-packed C_{60} fullerenes in $(C_{60})_{1.5}$(CTV); centroid-to-centroid distances: 10.00 –10.2 Å.[47]

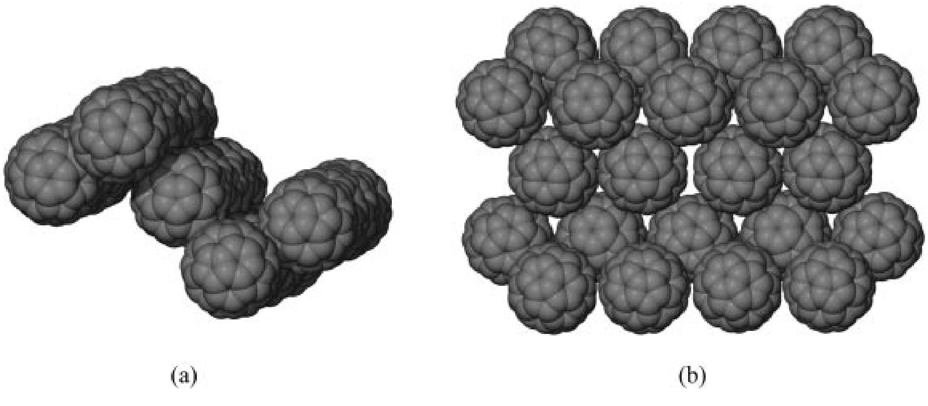


Figure 8. (a) Projection of the fivefold Z-shaped arrangement of fullerenes in $[(C_{60})_5\{\text{calix[5]arene}\}_4]$, and (b) the projection normal to this; closest centroid-to-centroid distances: 9.88 Å.[32]

Complexation of C_{60} in toluene solutions of CTV (**4**, R = R′ = Me) results in polymeric structures in the solid state, with either a fullerene-rich phase $(C_{60})_{1.5}$(CTV) or a 1:1 phase (C_{60})(CTV)[47,48] (Figure 9); both complexes were studied electrochemically (solution and solid state). The structures are dominated by fullerene···fullerene interactions, and each CTV has a C_{60} that is associated within the cavity of the CTV as a "ball and socket" nanostructure. For $(C_{60})_{1.5}$(CTV), the fullerenes collectively comprise a two-dimensional, close-packed array with half of the fullerenes devoid of CTV (Figure 9).[47] Disorder is found for the fullerenes that are not capped by CTV, while the fullerenes included in the cavity of CTV are stabilised and show order. Solvated host–guest species of (CTV)(C_{60}) are formed first in solution, and this results in the polarisation of the fullerene that promotes aggregation, which is evident by a resonant interfullerene transition band as 475 nm. Interestingly, C_{70} does not form an isolable complex with CTV, yet remarkably in the presence of 1,2-dicarborane, a ternary complex forms, with each fullerene in the cavity of a CTV molecule and with each of these supermolecules linked by bifurcated H-bonding to two carborane molecules, thus forming a helical arrangement. Therefore, additional synthons can encourage host–guest chemistry.[49]

Corrugated Sheets

C_{60} molecules can also form corrugated sheets in a manner that is similar to layering. In this arrangement, the C_{60} molecules form layers, but these layers are not planar. From a side-on view, these sheets look like zigzag arrangements. Corrugated sheets are also a common arrangement for C_{60} molecules, and a very high proportion of the compounds that exhibit this structure exhibit fullerene···fullerene close contacts, and this fact indicates that these molecules are at the van der Waals limits. Hence, it can be concluded that when C_{60} molecules are arranged in corrugated layers, as opposed to planar layers, close contact between the fullerenes is encouraged. Corrugated-sheet structures also have a high proportion of ordered compounds.

Non-aromatic macrocycles **5** have two divergent concave surfaces in a saddle-shape arrangement that arises from the otherwise unfavourable interactions between the methyl groups and the adjacent H-atoms on the aromatic rings. This arrangement can act as a divergent heterotopic receptor towards C_{60}. In the structure of (C_{60})Ni(TMTAA) (**5**, R = H, R′ = R′′ = Me), two host molecules shroud the fullerene such that a fullerene is in the saddle of one Ni(TMTAA) molecule with the methyl groups directed towards it and in the opposite saddle of another Ni(TMTAA) molecule; the overall host–guest contacts form a continuous zigzag array in which the fullerenes form a corrugated two-dimensional sheet (Figure 10).[50] Cu^{II} and Zn^{II} TMTAA molecules bind C_{60} in a similar fashion and are isostructural with the Ni^{II} analogue. OMTAA (**5**, R = Me) forms a 1:1 complex with C_{60} in which the extended supramolecular array is based on linear chains of close-contact C_{60} molecules and on linear chains of π-stacked alternating molecules of C_{60} and Ni(OMTAA) in which the adjacent chains run in opposite directions and thus cancel out the dipole moments. The same macrocycle forms a 1:1 complex with C_{70}, which is isostructural with the C_{60} complex of Ni(TMTAA). In all of these Ni^{II} macrocyclic structures, there are no significant contacts between the metal centres and the fullerenes. As in other systems, there is evidence for the formation of 1:1 solvated supermolecules in solution, which then go on to form micelle-like species.[50] The unsymmetrical macrocycle **5** (R = H, R′ = Me, R′′ = Ph) also forms a 1:1 complex with C_{60}.[51]

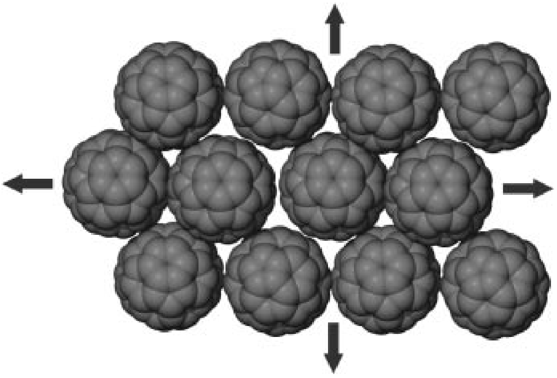


Figure 10. The corrugated array of fullerenes in the Ni(TMTAA)/C_{60} complex; centroid-to-centroid distances: 9.99 to10.07 Å.[50]

Honeycomb Motif

An unusual arrangement of the C_{60} molecules is one in which the fullerene molecules form a honeycomb motif as shown in Figure 11.[52] Few compounds exhibit this type of arrangement, and in most cases, these structures have disordered fullerenes.[36]

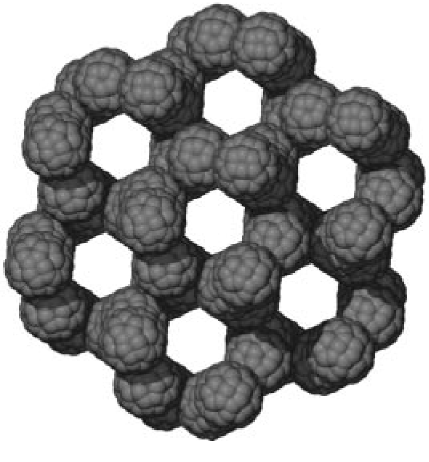


Figure 11. The honeycomb arrangement of C_{60} molecules in 5,10,15,20-tetraphenylporphyrin bis(C_{60}-fullerene) benzene solvate; centroid-to-centroid distances: 9.98 Å.[52]

3D Continuous Networks of C_{60}

The arrangement of fullerenes in fullerene-C_{60} complexes can have continuous three-dimensional networks. Some are simply analogues of the *fcc* packing of pristine C_{60}. Indeed, the simplest structure is one in which the *fcc* packing is maintained and small molecules are included in the interstices, for example ethene (Figure 12).[53] For larger molecules, other arrangements are possible. Alternatively, other close-packed arrangements can result, notably *bcc* packing found in the ethane complex.[53]

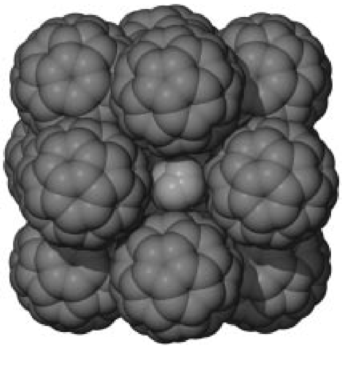


Figure 12. The *fcc* arrangement in the ethene inclusion complex with C_{60}; centroid-to-centroid distances: 10.03 Å.[53]

Other continuous three-dimensional arrangements are more complex, often, with more included molecules, for example, the carbon disulfide complex $C_{60}\cdot1.5CS_2$ (Figure 13).[54]

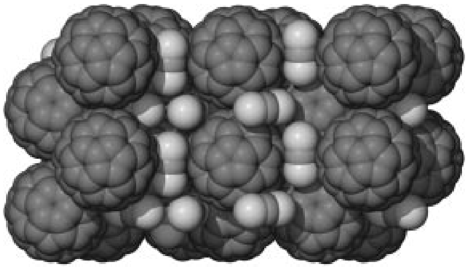


Figure 13. Continuous array in the C_{60}-fullerene carbon disulfide solvate ($C_{60}\cdot1.5CS_2$); closest centroid-to-centroid distances: 9.96 Å.[54]

From Table 1, it is evident that three-dimensional arrangements are more prevalent and by their very nature have more interfullerene contacts at the van der Waals limits. Intersecting sheets of fullerenes with moderately sized molecules creating channels are possible; this is exemplified by the structures in Figure 14.[55]

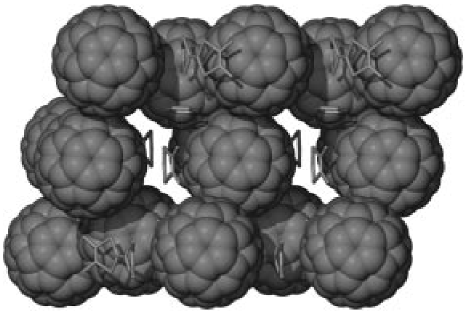


Figure 14. Structure of C_{60}-fullerene/tetramethyltetraselenafulvalene benzene solvate; centroid-to-centroid distances: 9.80 Å.[55]

Higher Complexity Structural Motifs

The structures here are based on complexes containing large host/included molecules. The fullerene rich calix[6]arene complexes, $(C_{60}/C_{70})_2$calix[6]arene, have been structurally authenticated as isomorphous complexes,[56] and exhibit the calixarene in a double-cone conformation and a fullerene perched in each of the shallow cavities – this arrangement resembles the jaws of a pincer acting on two adjacent cage molecules; the extended structures have continuous three-dimensional interplay of the fullerenes that is close to the van der Waals limit. In the case of the C_{70} complex, the principle axis of the fullerene is aligned such that the end of the fullerene that is close to this axis, where the curvature of the cage is similar to that of C_{60}, resides in the cavity.

Calix[4]arenes and Calix[4]resorcinarenes have cavities that are too small to accommodate fullerenes. Nevertheless, some calix[4]arenes have been shown to form stable crystalline complexes with C_{60} with the fullerene *exo* to the calixarene cavity, and include: (i) *p*-phenyl-calix[4]arene, which has a toluene molecule in the cavity; the overall structure is dominated by fullerene–fullerene and *exo*-calixarene–fullerene interactions,[57] (ii) *p*-bromo-calix[4]arene propyl ether – the structure shows very close interfullerene contacts in a columnar structure, which most likely results in opposing induced dipoles from the unidirectionally aligned calixarenes,[58] and (iii) *p*-iodo-calix[4]arene benzyl ether – the fullerenes are ordered without appreciable interfullerene interactions.[59] There is also calix[4]resorcinarene **3** (R = CH_2CH_2Ph), which has a molecular capsule derived from head-to-head hydrogen bonding of two resorcinarene and propan-2-ol molecules – the fullerenes are also arranged in columns.[60] Biscalix[4]resorcinare is effective in binding C_{60} (cf. biscalixarenes, Figure 4),[61] and calix[4]resorcinarenes (**3**) that bear dithiocarbamate groups between the oxo groups, with R = alkyl chains and with methylene groups between adjacent oxo groups form torus-shaped complexes that comprise three calixarenes with divalent cadmium and zinc ions, which effectively bind C_{60}.[62]

The fourfold symmetry of calixarenes and resorcinarenes relates to complexation of siloxane **8** with C_{60} in toluene.[49,59,60] Here, the fullerenes are arranged in double-columnar arrays and are shrouded by edge-on siloxanes – the siloxanes are interlocked by one of the phenyl groups of one molecule residing in the cavity of another.

Bulky groups incorporated into porphyrin **6** [R = H, R′ = C_6H_3-3,5-$(tBu)_2$] result in a 1:1 complex with C_{60}, but there is a fullerene on either side of the porphyrin such that the continuous structure has the fullerene encapsulated.[63]

Conclusion and Prospects

Structural analysis reveals a diverse range of structures; in some cases, these structures appear regularly, whilst others are represented by a single example. Even with prior knowledge on the composition of fullerene C_{60} complexes, it is difficult to predict the arrangement of fullerenes given the inherently weak interactions between the components and the delicate balance between fullerene···fullerene interactions and host···fullerene interactions. Predicting the outcome of crystallization with respect to host/guest ratios and the arrangement between the components is even more problematic, and this is compounded by the effect of other solutes on the complexes formed that are still not an integral part of the structure. Greater structural diversity is anticipated along with higher complexity of the structures, although full characterization of such complexes using diffraction data will be a major challenge. Compounds in which the C_{60} molecules are arranged in planar layers contain the highest levels of order of the fullerenes, and, in general, structures in which there is symmetry matching between the host and the fullerene reduces the disorder of the fullerene at low temperature. Arrays of fullerenes can be completely shrouded by a sheath of host molecules. The reverse is possible whereby the "host molecules" can reside in channels formed by a continuous array of fullerenes at the van der Waals limit. Clearly designing host molecules to bind fullerenes in cavities is now well established, but unless the fullerene is completely shrouded by host molecules, predicting the interplay of the fullerenes has serious limitations.

Acknowledgments

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[1] M. Jansen, G. Waidmann, *Z. Anorg. Allg. Chem.* **1995**, *621*, 14.

[2] R. E. Dinnebier, O. Gunnarsson, H. Brumm, E. Koch, P. W. Stephens, A. Huq, M. Jansen, *Science* **2002**, *296*, 109.

[3] J. D. Crane, P. B. Hitchcock, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.* **1992**, 1764.

[4] J. L. Atwood, G. A. Koutsantonis, C. L. Raston, *Nature* **1994**, *368*, 229; J. L. Atwood, L. J. Barbour, C. L. Raston, *Cryst. Growth Des.* **2002**, *2*, 3; T. Haino, Y. Yamanaka, H. Araki, Y. Fukazawa, *Chem. Commun.* **2002**, 402; J. Wang, S. G. Bodige, W. H. Watson, C. D. Gutsche, *J. Org. Chem.* **2000**, *65*, 8260.

[5] J. L. Atwood, M. J. Barnes, M. G. Gardiner, C. L. Raston, *Chem. Commun.* **1996**, 1449; J. L. Atwood, M. J. Barnes, R. S. Burkhalter, P. C. Junk, J. W. Steed, C. L. Raston, *J. Am. Chem. Soc.* **1994**, *116*, 10346; D. Felder, B. Heinrich, D. Guillon, J.-F. Nicoud, J.-F. Nierengarten, *Chem. Eur. J.* **2000**, *6*, 3501; H. Matsubara, S. Oguri, K. Asano, K. Yamamoto, *Chem. Lett.* **1999**, 431.

[6] T. Ishii, N. Aizawa, R. Kanehama, M. Yamashita, K. Sugiura, H. Miyasaka, *Coord. Chem. Rev.* **2002**, *226*, 113; A. L. Balch, M. M. Olmstead, *Coord. Chem. Rev.* **1999**, *185–186*, 601.

[7] D. Sun, C. A. Reed, *Chem. Commun.* **2000**, 2391–2392.

[8] J. L. Atwood, L. J. Barbour, M. W. Heaven, C. L. Raston, *Angew. Chem. Int. Ed.* **2003**, *42*, 3257.

[9] C. L. Raston, "Complexation of Fullerenes", in *Comprehensive Supramolecular Chemistry* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. Macnicol, F. Vögtle), Pergamon, Oxford, **1996**, vol. 1, 777–787; M. J. Hardie, C. L. Raston, *Chem. Commun.* **1999**, 1153–1163; T. Ishii, N. Aizawa, R. Kanehama, M. Yamashita, K. Sugiura, H. Miyasaka, *Coord. Chem. Rev.* **2002**, *226*, 113–124; F. Diederich, M. Gomez-Lopez, *Chem. Soc. Rev.* **1999**, *28*, 263–277; D. V. Konarev, R. N. Lyubovskaya, N. V. Drichko, *J. Mater. Chem.* **2000**, *10*, 803.

[10] S. Zhou, C. Burger, B. Chu, M. Sawamura, N. Nagahama, M. Toganoh, U. E. Hackler, H. Isobe, E. Nakamura, *Science* **2001**, *291*, 1944–1946.

[11] D. M. Guldi, N. Martin, *J. Mater. Chem.* **2002**, *12*, 1978–1992.

[12] D. V. Konarev, S. S. Khasanov, A. Otsuka, Y. Yoshida, G. Saito, *J. Am. Chem. Soc.* **2002**, *124*, 7648–7649.

[13] J. Ruiz, C. Pradet, F. Varret, D. Astruc, *Chem. Commun.* **2002**, 1108–1109.

[14] J. P. Majoral, A. M. Caminade, *Chem. Rev.* **1999**, *99*, 845–880; J. F. Nierengarten, L. Oswald, J. F. Eckert, J. F. Nicoud, N. Armaroli, *Tetrahedron Lett.* **1999**, *40*, 5681–5684.

[15] M. Ayabe, A. Ikeda, Y. Kubo, M. Takeuchi, S. Shinkai, *Angew. Chem. Int. Ed.* **2002**, *41*, 2790–2792; M. Kimura, Y. Saito, K. Hanabusa, H. Shiral, N. Kobayashi, *J. Am. Chem. Soc.* **2002**, *124*, 5274–5275.

[16] S. A. Jenekhe, X. L. Chen, *Science* **1998**, *279*, 1903–1906.

[17] M. J. Hardie, C. L. Raston, *Chem. Commun.* **1999**, 1153–1163.

[18] K. Moller, T. Bein, *Chem. Mater.* **1998**, *10*, 2950–2963.

[19] T. Okazaki, K. Suenaga, K. Hirahara, S. Banow, S. Iijima, H. Shinohara, *J. Am. Chem. Soc.* **2001**, *123*, 9673–9674.

[20] D. Sun, F. S. Tham, C. A. Reed, L. Chaker, P. D. W. Boyd, *J. Am. Chem. Soc.* **2002**, *124*, 6604.

[21] S. Mizyed, P. E. Geroghiou, M. Bancu, B. Cuadra, A. K. Rai, P. Cheng, L. T. Scott, *J. Am. Chem. Soc.* **2001**, *123*, 12770–12774.

[22] Y. Yamaguchi, S. Kobayashi, N. Amita, T. Wakamiya, *Tetrahedron Lett.* **2002**, *43*, 3277–3280.

[23] E. M. Veen, P. M. Postma, H. T. Jonkman, A. L. Spek, B. L. Feringa, *Chem. Commun.* **1999**, 1709–1710.

[24] A. Ikeda, Y. Suzuki, M. Yoshimura, S. Shinkai, *Tetrahedron* **1998**, *54*, 2497–2508.

[25] D. V. Konarev, A. Y. Kovalevsky, P. Coppens, R. N. Lyubovskaya, *Chem. Commun.* **2000**, 2358–2359.

[26] H.-B. Burgi, E. Blanc, D. Schwarzenbach, S. Liu, Y.-J. Lu, M. M. Kappes, J. A. Ibers, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 640.

[27] T. Ishii, N. Aizawa, R. Kanehama, M. Yamashita, H. Matsuzaka, T. Kodama, K. Kikuchi, I. kemoto, *Inorg. Chim. Acta* **2001**, *317*, 81; H. Matsubara, A. Hasegawa, K. Shiwaku, K. Asano, M. Uno, S. Takahashi, K. Yamamoto, *Chem. Lett.* **1998**, 923; S. Mizyed, M. Ashram, D. O. Miller, P. E. Georghiou, *J. Chem. Soc., Perkin Trans. 2* **2001**, 1916; D. V. Soldatov, P. R. Diamente, C. I. Ratcliffe, J. A. Ripmeester, *Inorg. Chem.* **2001**, *40*, 5660; M. M. Olmstead, D. A. Costa, K. Maitra, B. C. Noll, S. L. Phillips, P. M. Van Calcar, A. L. Balch, *J. Am. Chem. Soc.* **1999**, *121*, 7090; J. L. Atwood, L. J. Barbour, P. J. Nichols, C. L. Raston, C. A. Sandoval, *Chem. Eur. J.* **1999**, *5*, 990; A. L. Balch, M. M. Olmstead, *Coord. Chem. Rev.* **1999**, *1858*, 601; J. Wang, S. G. Bodige, W. H. Watson, C. D. Gutsche, *J. Org. Chem.* **2000**, *65*, 8260; D. V. Konarev, A. Y. Kovalevsky, X. Li, I. S. Neretin, A. L. Litvinov, N. V. Drichko, Y. L. Slovokhotov, P. Coppens, R. N. Lyubovskaya, *Inorg. Chem.* **2002**, *41*, 3638; T. Ishii, N. Aizawa, M. Yamashita, H. Matsuzaka, T. Kodama, K. Kikuchi, I. Ikemoto, Y. Iwasa, *J. Chem. Soc., Dalton Trans.* **2000**, 4407; E. Blanc, R. Restori, D. Schwarzenbach, H.-B. Burgi, M. Fortsch, P. Venugopalan, O. Ermer, *Acta Crystallogr., Sect. B: Struct. Sci.* **2000**, *56*, 1003; T. Ishii, R. Kanehama, N. Aizawa, M. Yamashita, H. Matsuzaka, K. Sugiura, H. Miyasaka, T. Kodama, K. Kikuchi, I. Ikemoto, H. Tanaka, K. Marumoto, S. Kuroda, *J. Chem. Soc., Dalton Trans.* **2001**, 2975; T. Haino, M. Yanase, Y. Fukazawa, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 259; V. V. Kveder, E. A. Steinman, B. Z. Narymbetov, S. S. Khasanov, L. P. Rozenberg, R. P. Shibaeva, A. V. Bazhenov, A. V. Gorbunov, M. Y. Maksimuk, D. V. Konarev, R. N. Lyubovskaya, Yu. A. Ossipyan, *Chem. Phys.* **1997**, *216*, 407; M. Jansen, G. Waidmann, *Z. Anorg. Allg. Chem.* **1995**, *621*, 14; K. N. Rose, L. J. Barbour, G. W. Orr, J. L. Atwood, *Chem. Commun.* **1998**, 407; D. H. Hochmuth, S. L. J. Michel, A. J. P. White, D. J. Williams, A. G. M. Barrett, B. M. Hoffman, *Eur. J. Inorg. Chem.* **2000**,

593; M. Fedurco, M. M. Olmstead, W. R. Fawcett, *Inorg. Chem.* **1995**, *34*, 390; N. G. Spitsina, V. V. Gritsenko, O. A. D'yachenko, B. B. Safoklov, Y. M. Shul'ga, E. B. Yagubskii, *Izv. Akad. Nauk SSSR, Ser. Khim.(Russ.) (Russ. Chem. Bull.)* **2000**, 365; A. L. Balch, K. Maitra, M. M. Olmstead, Private Communication, **2000**; A. Arrais, E. Diana, R. Gobetto, M. Milanesio, D. Viterbo, P. L. Stanghellini, *Eur. J. Inorg. Chem.* **2003**, 1186; L. J. Barbour, G. W. Orr, J. L. Atwood, *Chem. Commun.* **1997**, 1439; M. Makha, M. J. Hardie, C. L. Raston, *Chem. Commun.* **2002**, 1446.

[28] A. L. Litvinov, D. V. Konarev, R. N. Lyubovskaya, B. P. Tarasov, I. S. Neretin, Yu. L. Slovokhotov, *Synth. Met.* **2001**, *121*, 1119; T. Haino, M. Yanase, Y. Fukazawa, *Tetrahedron Lett.* **1997**, *38*, 3739; K. Tsubaki, K. Tanaka, T. Kinoshita, K. Fuji, *Chem. Commun.* **1998**, 895; D. Sun, F. S. Tham, C. A. Reed, L. Chaker, P. D. W. Boyd, *J. Am. Chem. Soc.* **2002**, *124*, 6604; P. D. W. Boyd, M. C. Hodgson, C. E. F. Rickard, A. G. Oliver, L. Chaker, P. J. Brothers, R. D. Bolskar, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **1999**, *121*, 10487; D. V. Konarev, A. Yu. Kovalevsky, X. Li, I. S. Neretin, A. L. Litvinov, N. V. Drichko, Y. L. Slovokhotov, P. Coppens, R. N. Lyubovskaya, *Inorg. Chem.* **2002**, *41*, 3638; T. Haino, M. Yanase, Y. Fukazawa, *Tetrahedron Lett.* **1997**, *38*, 3739.

[29] E. M. Veen, P. M. Postma, H. T. Jonkman, A. L. Spek, B. L. Feringa, *Chem. Commun.* **1999**, 1709; L. J. Barbour, G. W. Orr, J. L. Atwood, *Chem. Commun.* **1998**, 1901; A. L. Litvinov, D. V. Konarev, A. Y. Kovalevsky, I. S. Neretin, Yu. L. Slovokhotov, P. Coppens, R. N. Lyubovskaya, *CrystEngComm* **2002**, *4*, 618; L. Golic, R. Blinc, P. Cevc, D. Arcon, D. Mihailovic, A. Omerzu, P. Venturini, *Proc. 10th Int. Winter. Electron Prop. Novel Mater.* **1996**, 531; B. Narymbetov, H. Kobayashi, M. Tokumoto, A. Omerzu, D. Mihailovic, *Chem. Commun.* **1999**, 1511; K. Tanaka, M. R. Caira, *J. Chem. Res.* **2002**, 642; D. M. Eichhorn, S. Yang, W. Jarrell, T. F. Baumann, L. S. Beall, A. J. P. White, D. J. Williams, A. G. M. Barrett, B. M. Hoffman, *Chem. Commun.* **1995**, 1703.

[30] M. M. Olmstead, D. A. Costa, K. Maitra, B. C. Noll, S. L. Phillips, P. M. Van Calcar, A. L. Balch, *J. Am. Chem. Soc.* **1999**, *121*, 7090; D. H. Hochmuth, S. L. J. Michel, A. J. P. White, D. J. Williams, A. G. M. Barrett, B. M. Hoffman, *Eur. J. Inorg. Chem.* **2000**, 593; J. L. Atwood, M. J. Barnes, M. G. Gardiner, C. L. Raston, *Chem. Commun.* **1996**, 1449; D. V. Konarev, I. S. Neretin, Y. L. Slovokhotov, E. I. Yudanova, N. V. Drichko, Y. M. Shul'ga, B. P. Tarasov, L. L. Gumanov, A. S. Batsanov, J. A. K. Howard, R. N. Lyubovskay, *Chem. Eur. J.* **2001**, *7*, 2605; H. M. Lee, M. M. Olmstead, T. Suetsuna, H. Shimotani, N. Dragoe, R. J. Cross, K. Kitazawa, A. L. Balch, *Chem. Commun.* **2002**, 1352; S. I. Troyanov, E. Kemnitz, *Zh. Neorg. Khim. (Russ.) (Russ. J. Inorg. Chem.)* **2001**, *46*, 1704; O. A. D'yachenko, S. V. Konovalikhin, *Koord. Khim. (Russ.) (Coord. Chem.)* **1998**, *24*, 700; D. V. Konarev, I. S. Neretin, Y. L. Slovokhotov, E. I. Yudanova, N. V. Drichko, Y. M. Shul'ga, B. P. Tarasov, L. L. Gumanov, A. S. Batsanov, J. A. K. Howard, R. N. Lyubovskay, *Chem. Eur. J.* **2001**, *7*, 2605; B. Z. Narymbetov, S. S. Khasanov, L. V. Zorina, L. P. Rozenberg, R. P. Shibaeva, D. V. Konarev, R. N. Lyubovskaya, *Kristallografiya (Russ.) (Crystallogr. Rep.)* **1997**, *42*, 851.

[31] I. E. Grey, M. J. Hardie, T. J. Ness, C. L. Raston, *Chem. Commun.* **1999**, 1139; M. M. Olmstead, A. S. Ginwalla, B. C. Noll, D. S. Tinti, A. L. Balch, *J. Am. Chem. Soc.* **1996**, *118*, 7737; A. Izuoka, T. Tachikawa, T. Sugawara, Y. Saito, H. Shinohara, *Chem. Lett.* **1992**, 1049; A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito, H. Shinohara, *Chem. Commun.* **1992**, 1472.

[32] J. L. Atwood, L. J. Barbour, C. L. Raston, *Cryst. Growth Des.* **2002**, *2*, 3.

[33] M. V. Korobov, A. L. Mirakian, N. V. Avramenko, E. F. Valeev, I. S. Neretin, Y. L. Slovokhotov, A. L. Smith, G. Oloffson, R. S. Ruoff, *J. Phys. Chem. B* **1998**, *102*, 3712; A. L. Litvinov, D. V. Konarev, A. Y. Kovalevsky, I. S. Neretin, Y. L. Slovokhotov, P. Coppens, R. N. Lyubovskaya, *CrystEngComm* **2002**, *4*, 618; U. Geiser, S. Kalyan Kumar, B. M. Savall, S. S. Harried, K. D. Carlson, P. R. Mobley, H. Wang, J. M. Williams, R. E. Botto, W. Liang, M.-H. Whangbo, *Chem. Mater.* **1992**, *4*, 1077; S. V. Konovalikhin, O. A. D'yachenko, G. V. Shilov, N. G. Spitsina, K. V. Van, E. B. Yagubskii, *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ.) (Russ. Chem. Bull.)* **1997**, 1480; R. E. Marsh, M. Kapon, S. Hu, F. H. Herbstein, *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 62; D. V. Konarev, A. Yu. Kovalevsky, P. Coppens, R. N. Lyubovskaya, *Chem. Commun.* **2000**, 2357; E. M. Veen, P. M. Postma, H. T. Jonkman, A. L. Spek, B. L. Feringa, *Chem. Commun.* **1999**, 1709; D. V. Konarev, E. F. Valeev, Y. L. Slovokhotov, Y. M. Shul'ga, R. N. Lyubovskaya, *J. Chem. Res.* **1997**, *442*, 2647.

[34] A. M. Bond, W. Miao, C. L. Raston, T. J. Ness, M. J. Barnes, J. L. Atwood, *J. Phys. Chem. B* **2001**, *105*, 1687; J. D. Crane, P. B. Hitchcock, H. W. Kroto, R. Taylor, D. R. M. Walton, *Chem. Commun.* **1992**, 1764; N. G. Spitsyna, S. V. Konovalikhin, A. S. Lobach, G. V. Shilov, O. A. D'yachenko, *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ.) (Russ. Chem. Bull.)* **1999**, 2298; V. A. Nadtochenko, V. V. Gritsenko, O. A. Dyachenko, G. V. Shilov, A. P. Moravsky, *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ.) (Russ. Chem. Bull.)* **1996**, 1285.

[35] T. Ishii, N. Aizawa, R. Kanehama, M. Yamashita, H. Matsuzaka, T. Kodama, K. Kikuchi, I. Ikemoto, *Inorg. Chim. Acta* **2001**, *317*, 81; A. L. Litvinov, D. V. Konarev, A. Y. Kovalevsky, I. S. Neretin, Y. L. Slovokhotov, P. Coppens, R. N. Lyubovskaya, *CrystEngComm* **2002**, *4*, 618; G. Waidmann, M. Jansen, *Z. Naturforsch. B: Chem. Sci.* **1998**, *53*, 161; T. Ishii, N. Aizawa, M. Yamashita, H. Matsuzaka, T. Kodama, K. Kikuchi, I. Ikemoto, Y. Iwasa, *J. Chem. Soc., Dalton Trans.* **2000**, 4407; R. Schwenninger, J. Schlogl, J. Maynollo, K. Gruber, P. Ochsenbein, H.-B. Burgi, R. Konrat, B. Krautler, *Chem. Eur. J.* **2001**, *7*, 2676; N. G. Spitsina, V. V. Gritsenko, M. G. Kaplunov, O. A. D'yachenko, E. G. Yagubsky, *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ.) (Russ. Chem. Bull.)* **2001**, 1354; P. C. Andrews, J. L. Atwood, L. J. Barbour, P. D. Croucher, P. J. Nichols, N. O. Smith, B. W. Skelton, A. H. White, C. L. Raston, *J. Chem. Soc., Dalton Trans.* **1999**, 2927.

[36] D. V. Konarev, I. S. Neretin, Y. L. Slovokhotov, E. I. Yudanova, N. V. Drichko, Y. M. Shul'ga, B. P. Tarasov, L. L. Gumanov, A. S. Batsanov, J. A. K. Howard, R. N. Lyubovskaya, *Chem. Eur. J.* **2001**, *7*, 2605; E. M. Veen, P. M. Postma, H. T. Jonkman, A. L. Spek, B. L. Feringa, *Chem. Commun.* **1999**, 1709; M. F. Meidine, P. B. Hitchcock, H. W. Kroto, R. Taylor, D. R. M. Walton, *Chem. Commun.* **1992**, 1534; A. L. Balch, J. W. Lee, B. C. Noll, M. M. Olmstead, *Chem. Commun.* **1993**, 56; H. B. Burgi, R. Restori, D. Schwarzenbach, A. L. Balch, J. W. Lee, B. C. Noll, M. M. Olmstead, *Chem. Mater.* **1994**, *6*, 1325.

[37] P. R. Birkett, C. Christides, P. B. Hitchcock, H. W. Kroto, K. Prassides, R. Taylor, D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2* **1993**, 1407; A. O'Neil, C. Wilson, J. M. Webster, F. J. Allison, J. A. K. Howard, M. Poliakoff, *Angew. Chem. Int. Ed.* **2002**, *41*, 3796; A. Penicaud, O. Y. Carreon, A. Perrier, D. J. Watkin, C. Coulon, *J. Mater. Chem.* **2002**, *12*, 913; J. C. A. Boeyens, M. Ramm, D. Zobel, P. Luger, *S. Afr. J. Chem.* **1997**, *50*, 28; M. M. Olmstead, F. Jiang, A. L. Balch, *Chem. Commun.* **2000**, 483; A. I. Kotov, S. V. Konovalikhin, R. V. Pisarev, G. V. Shilov, O. A. Dyachenko, E. B. Yagubskii, *Mendeleev Commun.* **1994**, 180; A. Penicaud, K. Boubekeur, A. I. Kotov, E. B. Yagubskii, *Acta Crystallogr., Sect. B: Struct. Sci.* **2000**, *56*, 497; S. Margadonna, E. Aslanis, W. Z. Li, K. Prassides, A. N. Fitch, T. C. Hansen, *Chem. Mater.* **2000**, *12*, 2736; M. Ramm, P. Luger, W. Duczek, J. C. A. Boyens, *Cryst. Res. Technol.* **1996**, *31*, 43; W. Bensch, H. Werner, H. Bartl, R. Schlogl, *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2791; L. I. Buravov, O. A. D'yachenko, S. V. Konovalikhin, N. D. Kushch, I. P. Lavrent'ev, N. G. Spitsyna, G. V. Shilov, E. B. Yagubskii, *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ.) (Russ. Chem. Bull.)* **1994**, 262;

G. Roth, P. Adelmann, *Appl. Phys. A: Solids and Surfaces* **1993**, *56*, 169; P. D. Croucher, P. J. Nichols, C. L. Raston, *J. Chem. Soc., Dalton Trans.* **1999**, 279; A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito, H. Shinohara, *Chem. Commun.* **1992**, 1472; K. Tsubaki, K. Tanaka, T. Kinoshita, K. Fuji, *Chem. Commun.* **1998**, 895.

[38] J. L. Atwood, L. J. Barbour, P. J. Nichols, C. L. Raston, C. A. Sandoval, *Chem. Eur. J.* **1999**, *5*, 990.

[39] A. M. Bond, W. Miao, C. L. Raston, C. A. Sandoval, *J. Phys. Chem. B.* **2000**, *104*, 8129–8137.

[40] M. Makha, M. J. Hardie, C. L. Raston, *Chem. Commun.* **2002**, 1446–1447.

[41] T. Haino, M. Yanase, Y. Fukuzawa, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 259–260; T. Haino, M. Yanase, Y. Fukazawa, *Tetrahedron Lett.* **1997**, *38*, 3739–3742.

[42] C. L. Raston, J. L. Atwood, P. J. Nichols, I. B. N. Sudria, *Chem. Commun.* **1996**, *23*, 2615–2616.

[43] K. Tsubaki, K. Tanaka, T. Kinoshita, K. Fuji, *Chem. Commun.* **1998**, 895.

[44] A. L. Litvinov, D. V. Konarev, A. Yu. Kovalevsky, I. S. Neretin, Yu. L. Slovokhotov, P. Coppens, R. N. Lyubovskaya, *CrystEngComm* **2002**, *4*, 618.

[45] I. E. Grey, M. J. Hardie, T. J. Ness, C. L. Raston, *Chem. Commun.* **1999**, 1139.

[46] M. J. Hardie, C. L. Raston, *Chem. Commun.* **1999**, 1153–1163.

[47] A. M. Bond, W. Miao, C. L. Raston, T. J. Ness, M. J. Barnes, J. L. Atwood, *J. Phys. Chem. B* **2001**, *105*, 1687–1695.

[48] J. L. Atwood, M. J. Barnes, M. G. Gardiner, C. L. Raston, *Chem. Commun.* **1996**, 1449–1450.

[49] M. J. Hardie, P. D. Godfrey, C. L. Raston, *Chem. Eur. J.* **1999**, *5*, 1828–1833.

[50] P. C. Andrews, J. L. Atwood, L. J. Barbour, P. J. Nichols, C. L. Raston, *Chem. Eur. J.* **1998**, *4*, 1384.

[51] D. V. Soldatov, P. R. Diamente, C. I. Ratcliffe, J. A. Ripmeester, *Inorg. Chem.* **2001**, *40*, 5660.

[52] D. V. Konarev, I. S. Neretin, Y. L. Slovokhotov, E. I. Yudanova, N. V. Drichko, Y. M. Shul'ga, B. P. Tarasov, L. L. Gumanov, A. S. Batsanov, J. A. K. Howard, R. N. Lyubovskaya, *Chem. Eur. J.* **2001**, *7*, 2605.

[53] A. O'Neil, C. Wilson, J. M. Webster, F. J. Allison, J. A. K. Howard, M. Poliakoff, *Angew. Chem. Int. Ed.* **2002**, *41*, 3796.

[54] M. M. Olmstead, F. Jiang, A. L. Balch, *Chem. Commun.* **2000**, 483.

[55] O. A. D'yachenko, S. V. Konovalikhin, *Koord. Khim. (Russ.) (Coord. Chem.)* **1998**, *24*, 700.

[56] J. L. Atwood, L. J. Barbour, C. L. Raston, I. B. N. Sudria, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 981.

[57] S. Mizyed, P. R. Tremaine, P. E. Georghiou, *J. Chem. Soc., Perkin Trans. 2* **2001**, 3–6.

[58] L. J. Barbour, G. W. Orr, J. L. Atwood, *Chem. Commun.* **1998**, 1901–1902.

[59] J. Barbour, G. W. Orr, J. L. Atwood, *Chem. Commun.* **1997**, 1439–1440.

[60] K. N. Rose, L. J. Barbour, G. W. Orr, J. L. Atwood, *Chem. Commun.* **1998**, 407.

[61] Y. Wan, O. Mitkin, L. Barnhurst, A. Kurchan, A. Kutateladze, *Org. Lett.* **2000**, *2*, 3817–3819.

[62] G. D. Fox, M. G. B. Drew, E. J. S. Wilkinson, P. D. Beer, *Chem. Commun.* **2000**, 391–392.

[63] D. V. Konarev, I. S. Neretin, Y. L. Slovokhotov, E. I. Yudanova, N. V. Drichko, Y. M. Shul'ga, B. P. Tarasov, L. L. Gumanov, A. S. Batsanov, J. A. K. Howard, R. N. Lyubovskay, *Chem. Eur. J.* **2001**, *7*, 2605.

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