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New Host Architecture of Hydroquinone with Enclathrated C_{70}

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Abstract: The room-temperature crystal structure of a molecular 1:4.5:1 complex of C_{70}, hydroquinone (HQ), and benzene (bz), $C_{70}(HQ)_{4.5}bz$, is reported. The solid-state architecture of the donor–acceptor complex has trigonal symmetry and consists of a novel H-bonded superoctahedral HQ host network with three different types of cavities enclathrating the C_{70} and bz guest molecules. Giant HQ twin cages shaped according to the shell of a peanut house a pair of C_{70} molecules, large single cages accommodate one C_{70} guest, and smaller HQ cages of tetrahedral shape embrace a sandwich pair of bz molecules. The long axes of the C_{70} guest molecules are orthogonal to the trigonal crystal and cage axes. Their HQ host cages may be viewed as expanded supercubes and related to the simple supercube cavities of the sister complex $C_{60}(HQ)_3$ reported previously. A topological analogy exists between the tetrahedral HQ cages and the supertetrahedral building blocks of the pyrochlore network. The HQ host network of $C_{70}(HQ)_{4.5}bz$ is essentially ordered, and the C_{70} and bz guest species are orientationally disordered. The adopted benzene guest model is provisional only and requires further backing.

Hydroquinone (HQ) forms a 3:1 donor–acceptor complex with C_{60} involving a superoctahedral, hydrogen-bonded HQ host architecture.[2] This rhombohedral host framework may be reduced to the structural archetypes of polonium and ReO_3, respectively, through replacing the octahedrally coordinated metal atoms by H-bonded $(OH)_6$ rings linked up to the 3-dimensional (3D) HQ host network via covalent *p*-phenylene bridges. The network consists of "supercubes" with large cavities accommodating the spherical C_{60} guest molecules. We have now found that HQ forms a donor–acceptor complex with C_{70} as well, the crystal structure of which is reported here. Like $C_{60}(HQ)_3$, the C_{70}–HQ solid-state inclusion compound also possesses a superoctahedral HQ host network held together by hydrogen bonds, which in addition, however, enclathrates guest molecules of benzene (bz) used as the solvent for crystallization. The stoichiometry of the new complex is $C_{70}(HQ)_{4.5}bz_x$, with $x \simeq 1$. Expectedly,[2] the structure of the (expanded) HQ host cavities accommodating the C_{70} molecules deviates from the simple cube-shaped geometry encountered in $C_{60}(HQ)_3$ but such that topological interrelations are maintained in terms of common cube substructures. The benzene guest molecules are housed in separate smaller HQ host cages of tetrahedral shape.

Results and Discussion

The complex $C_{70}(HQ)_{4.5}bz$ crystallizes in the trigonal space group $P\bar{3}m1$ with four formula units in the cell. The related inclusion compound $C_{60}(HQ)_3$[2] adopts the rhombohedral space group $R\bar{3}m$, immediately suggesting structural correspondence with the present case: $P\bar{3}m1$ is a subgroup of $R\bar{3}m$ ("klassengleich" of index 3;[3] note that the hexagonal cell of $R\bar{3}m$ is 3-fold primitive, that of lower symmetric $P\bar{3}m1$ only 1-fold). The hexagonal cell constants of the C_{60}–HQ and C_{70}–HQ complexes may also be recognized as related, inviting more specific comparative structural contemplation; see the Experimental Section. The unit cell of the present C_{70}–HQ complex thus contains 4 molecules of C_{70}, 18 of HQ, and (approximately) 4 of benzene. The C_{70} molecules are grouped in two crystallographically nonequivalent pairs (types A and B, respectively; Figure 1), in both cases around C_{3v} sites. In view of their molecular D_{5h} symmetry, both independent C_{70} species are thus orientationally disordered, however, such that their long molecular 5-fold axes are in both cases perpendicular to the trigonal crystal axis *c*. The various statistical orientations of the C_{70} molecules are related by rotations around (average) crystallographic C_3 axes and very probably also through rotations around the molecular long (C_5) axes. The HQ molecules are grouped in three sets of six members each (types 1, 2, and 3; Figures 1 and 3), all with crystallographic C_s symmetry: types 1 and 2 with the mirror plane containing the C–O bonds and perpendicular to the molecular planes and type 3 with the mirror plane perpendicular to the long HQ O–O axis. The enclathrated benzene molecules are less well characterized crystallographically; they are grouped around a C_{3v} site (see figures) and, like the C_{70} guest molecules, are orientationally disordered, although not a priori enforced by symmetry constraints (oblique orientation of the bz planes with respect to the 3-fold axis).

The HQ host architecture of the present complex $C_{70}(HQ)_{4.5}bz$ is built up of hydrogen-bonded $(OH)_6$ rings covalently linked by the linear *p*-phenylene units to create a single 3-dimensional, highly porous network, in which the C_{70} and benzene guest molecules are embedded. The host network may be referred to as distorted superoctahedral and represents a new, fourth type of a 3D 6-connected net. A network pattern of this type may also be represented as an assembly of coordination octahedra (as done in many inorganic structural chemical studies) linked exhaustively and exclusively via sharing of vertices (MX_3-type structures with M denoting a metal atom and X oxygen or fluorine). The vertices of these octahedra would in the present HQ network be given by the midpoints of the six HQ *p*-phenylene bridging units emanating from the $(OH)_6$ rings playing the role of the octahedra's centers. Known other variants of 3D 6-connected nets are only three in number: (1) the simple cubic primitive polonium net with cube-shaped cages, similarly ReO_3 and the perowskites with octahedral metal centers bridged by divalent oxygen; (2) the tungsten bronzes; and (3) the pyrochlore-type structures (see below).[4] As already indicated, the octahedral network points of $C_{70}(HQ)_{4.5}bz$ are represented by the $(OH)_6$ rings from which six *p*-phenylene bridges radiate in a distorted octahedral disposition.

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[1] This work was supported by the Fonds der Chemischen Industrie.

[2] Ermer, O. *Helv. Chim. Acta* **1991**, *74*, 1339.

[3] *International Tables for Crystallography*, 2nd ed.; Hahn, T., Ed.; D. Reidel: Dordrecht, 1987; Vol. A: *Space Group Symmetry*.

[4] Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, 1987.

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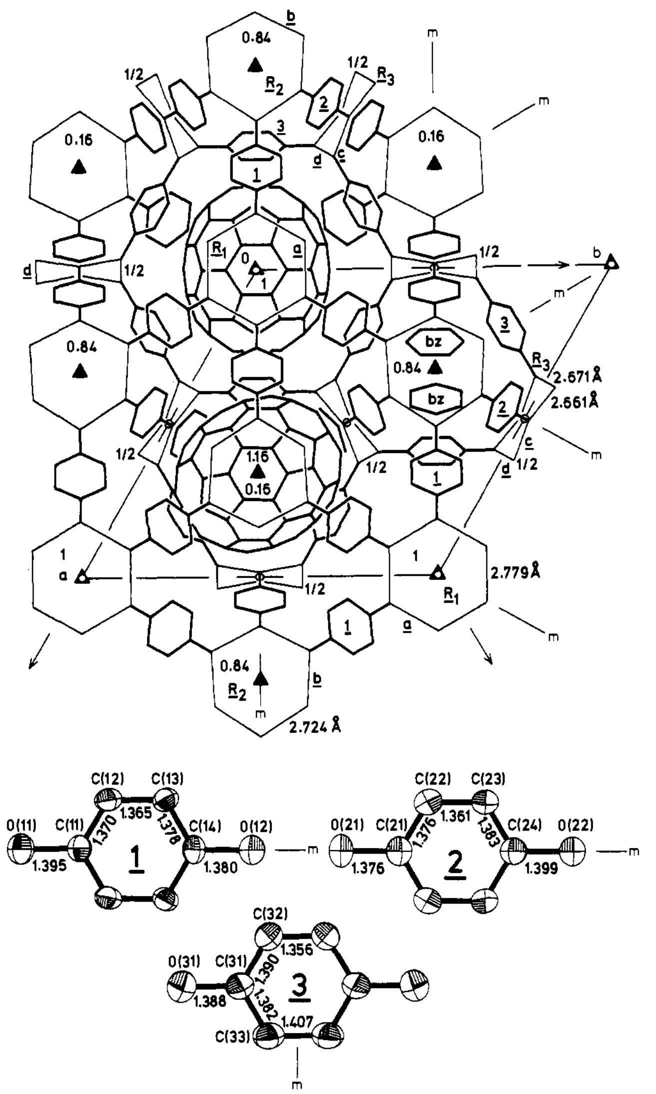

Figure 1. (Above) Space-group symmetry ($P\bar{3}m1$) diagram of $C_{70}(HQ)_{4.5}$bz projected along the trigonal crysta axis *c*; origin shifted by $^{c}/_{2}$ with respect to the coordinates of Table I. The elements forming the three different H-bonded HQ host cages $\underline{K}_1$, $\underline{K}_2$, and $\underline{K}_3$ are shown together with the guest species: large twin cage $\underline{K}_1$ around the origin (top left) with one type $\underline{A}$ C_{70} guest molecule drawn, second C_{70} guest obscured; medium-size single cage $\underline{K}_2$ around C_3 axis at $^2/_3$, $^1/_3$, *z* with type $\underline{B}$ C_{70} guest; smaller, approximately tetrahedral cage $\underline{K}_3$ around C_3 at $^1/_3$, $^2/_3$, *z* with enclathrated dimeric benzene sandwich. A single orientation is drawn of the guest molecules, which in fact are orientationally disordered to satisfy on average the space-group symmetry. The superoctahedral HQ host network is spanned by the H-bonded $(OH)_6$ rings (thin lines) and the covalent HQ *p*-phenylene connectors. A selection of point-symmetry elements is shown, and the heights of the $(OH)_6$ rings are given in units of the *c* edge length. The various types of HQ molecules, $(OH)_6$ rings, and hydrogen bonds (with O···O distances) are labeled with the respective symbols underlined. (Below) Vibrational ellipsoids (30%), bond lengths (Å), and atomic numbering of the three different types of HQ molecules; H atoms omitted. Estimated average standard deviation of interatomic distances given is ca. 0.008 Å.

A diagrammatic view of the network is shown in Figure 2. Three symmetry-different $(OH)_6$ rings are present with D_{3d}, C_{3v}, and C_{2h} symmetry (types $\underline{R}_1$, $\underline{R}_2$, and $\underline{R}_3$; Figures 1–3). Type $\underline{1}$ HQ molecules connect $\underline{R}_1$ and $\underline{R}_2$ $(OH)_6$ rings, type $\underline{2}$ HQs link $\underline{R}_2$ and $\underline{R}_3$, and type $\underline{3}$ HQs join pairs of equivalent rings $\underline{R}_3$. All three types of H-bonded $(OH)_6$ rings take up markedly puckered chair "superconformations" (Figure 4). According to their symmetry, type $\underline{R}_1$ and $\underline{R}_2$ rings have their mean planes oriented perpendicular to the trigonal *c* axis. On the other hand, the planes of the $\underline{R}_3$ rings are roughly at right angles with respect to those of $\underline{R}_1$ and $\underline{R}_2$ (Figure 1). Altogether, four nonequivalent types of O(H)O hydrogen bonds may be differentiated (types $\underline{a}$, $\underline{b}$, $\underline{c}$, and $\underline{d}$ with average site symmetries of C_2, C_1, C_1, and C_2; Figure 1). Without exception, they are 2-fold orientationally disordered, with O···O distances in the normal range 2.661–2.779 Å; individual values may be read from Figure 1. The higher symmetric host–guest architecture of $C_{60}(HQ)_3$ is much simpler:[2] one type each of C_{60} guest molecules, HQ host molecules, $(OH)_6$ rings, and O(H)O hydrogen bonds on average high-symmetry sites of D_{3d}, C_{2h}, D_{3d}, and C_2 symmetry, respectively. Accordingly, the host cavities of $C_{60}(HQ)_3$ are all equivalent and take up a simple supercube shape of D_{3d} symmetry (Figure 3d).

The HQ host network of the present complex $C_{70}(HQ)_{4.5}$bz is extremely porous and, without the C_{70} (and benzene) guest species, would have a density of only 0.54 g cm^{-3} as compared to 1.55 g cm^{-3} applying to the complete host–guest assembly. Three different categories of H-bonded cavities, denoted $\underline{K}_1$, $\underline{K}_2$, and $\underline{K}_3$, may be identified in the HQ host architecture of the C_{70} complex: (1) huge cages $\underline{K}_1$ of D_{3d} symmetry housing at once two C_{70} clusters of type $\underline{A}$ (see figures), (2) medium-size cages $\underline{K}_2$ of symmetry C_{3v} accommodating a single C_{70} football of type $\underline{B}$ and (3) smaller cages $\underline{K}_3$ of symmetry C_{3v} enclathrating (probably) two benzene molecules. The stoichiometric ratio of the number of cavities within the infinite H-bonded 3D network of HQ extending through the entire crystal is $\underline{K}_1$:$\underline{K}_2$:$\underline{K}_3$ = 1:2:2. In the following three paragraphs, the three different cavity variants are characterized in some detail, together with their molecular guests. The figures, in particular the full stereoviews of Figure 4, serve to illustrate the discussion.

The large double cage, type $\underline{K}_1$ of symmetry D_{3d}, requires the participation, i.e., the cooperation, of altogether 14 $(OH)_6$ rings and 24 *p*-phenylene units. The two polar caps of $\underline{K}_1$ centered on a trigonal C_3 axis represent distorted supercube sections and are joined via an equatorial macroring of six H-bonded type $\underline{3}$ HQ molecules; Figure 3a provides a diagrammatic view. This latter macroring establishes a kind of a waist, so to speak, partitioning the double cage into equivalent upper and lower halves (Figure 4a). The overall shape of $\underline{K}_1$ may aptly be likened to the shell of a peanut with the two connected compartments occupied by one C_{70} molecule each, such that the long molecular axis of C_{70} and the long trigonal axis of the twin cage are at right angles. (Peanuts prefer a more oblique orientation within their twin-cage shell.) The centers of the two type $\underline{A}$ C_{70} molecules within the same HQ twin cage are only 10.10 Å apart, and both guests thus benefit from almost optimal contact in the equatorial plane of the six type $\underline{3}$ HQ molecules forming the above-mentioned waist. Obviously, this short C_{70}–C_{70} contact is further improved by the orthogonal orientation of the C_{70} rotational ellipsoids with respect to the long twin-cage axis, since in this way, the C_{70} guests touch under minimum possible convex curvature. Apart from the narrow C_{70}–C_{70} contact, each C_{70} molecule in the twin cage $\underline{K}_1$ is involved in six face-to-face (FF) and nine edge-to-face (EF) contacts with the enclathrating HQ molecules: three FF with HQ (type $\underline{1}$), three FF with HQ($\underline{3}$), six EF with HQ($\underline{2}$), and three EF with HQ($\underline{3}$). The respective distances between the centers of gravity of C_{70} and the contacting HQ ligands amount in this sequence to 6.97, 7.06, 8.63, and 8.63 Å. The six HQ($\underline{3}$) molecules of the equatorial waist macroring simultaneously provide three FF and three EF alternating contacts each with the upper and lower C_{70} guest, respectively, in the double cage; see Figure 4a. In $C_{60}(HQ)_3$,[2] the C_{60} spheres are confined in D_{3d} HQ supercube single cages and experience six equivalent FF and six equivalent EF contacts with the HQ host molecules. The increased number of host–guest contacts in the present C_{70} complex accounts for the increased surface of C_{70} as compared to that of C_{60}. In essence, the basic structural principle of the large D_{3d} double "peanut cage" $\underline{K}_1$ may be reduced to a cube with its six equatorial vertices truncated, which are grouped around a C_3 space diagonal.

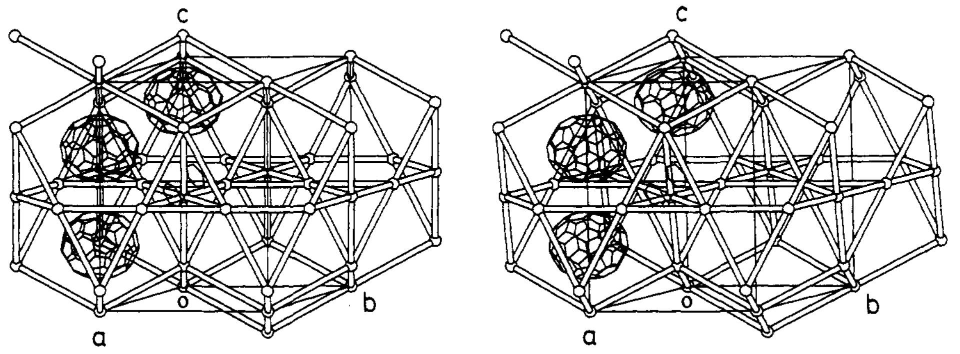

Figure 2. Diagrammatic stereorepresentation of the H-bonded superoctahedral HQ host network of $C_{70}(HQ)_{4.5}bz$ with line drawings of guest molecules; cell edges outlined. The spheres symbolize the $(OH)_6$ rings (at their midpoints) acting as octahedral centers, and the thick rods stand for the interconnecting HQ *p*-phenylene bridges. A twin cage, $\underline{K}_1$ (left), is shown with its two type $\underline{A}$ C_{70} guests, a single cage, $\underline{K}_2$ (top), with its one type $\underline{B}$ C_{70} guest, and a tetrahedral cage, $\underline{K}_3$ (front center), with the dimeric benzene guest sandwich. Single orientations of the actually disordered guest molecules are shown.

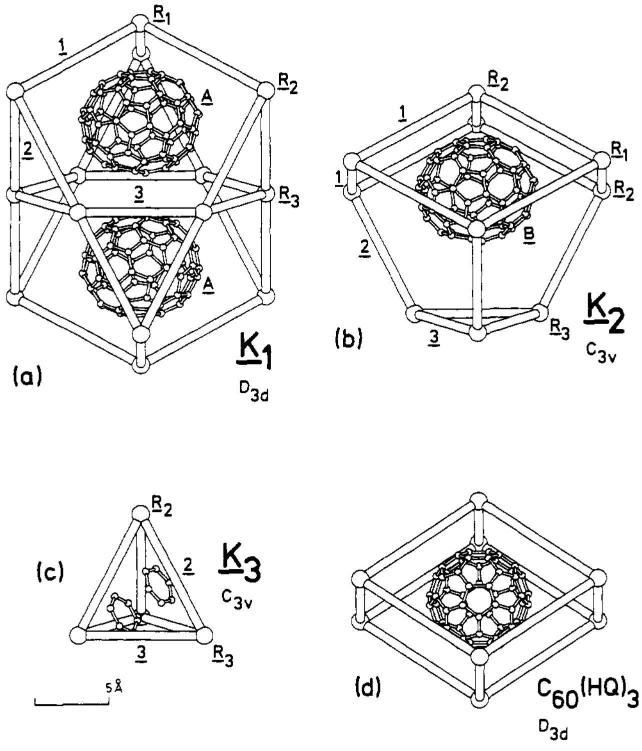

Figure 3. Diagrammatic views of the three H-bonded HQ host cages of $C_{70}(HQ)_{4.5}bz$ together with ball-and-stick models of the guest molecules and a view of the cage of $C_{60}(HQ)_3$. Representation and views are the same as in Figure 2 (see respective legend), i.e., large spheres represent the centers of the $(OH)_6$ rings and thick rods the *p*-phenylene connectors; the diagrams are cut out of the network of Figure 2 as oriented in the left-hand member of the stereopair. Labels of the various types of structural entities are shown (underlined, compare Figure 1) and the crystallographic symmetries of the cages indicated: (a) twin peanut cage $\underline{K}_1$ with two type $\underline{A}$ C_{70} guest clusters, (b) single cage $\underline{K}_2$ with type $\underline{B}$ C_{70} guest, (c) tetrahedral cage $\underline{K}_3$ with dimeric sandwich model of benzene guest pair, and (d) supercube cage of $C_{60}(HQ)_3$,[2] for comparison. All diagrams are drawn to the same scale. Note that the mode of abstraction chosen for representing the H-bonded HQ cages leads to the following artificial pictorial distortions: (a) for cage $\underline{K}_1$, the waist nature of the equatorial macroring formed by six H-bonded type $\underline{3}$ HQ molecules does not emerge, (b) the lower section of cage $\underline{K}_2$ looks too large and hollow, and (c) cage $\underline{K}_3$ appears too small. Impressions of the real host–guest dimensions are conveyed by the less easily surveilable "unabridged" Figure 1 and, in particular, by Figure 4.

In this (idealized) abstraction, the $(OH)_6$ rings are reduced to polyhedral vertices and the *p*-phenylene linkers to edges; Figure 3a provides an appropriate illustration. The twin cage $\underline{K}_1$ may thus conceptually be developed out of the simple HQ supercube single cage of $C_{60}(HQ)_3$ by elongation along the trigonal space diagonal and equatorial interposition of the waist of six additional HQ($\underline{3}$) molecules (Figures 3a,d).

The medium-size cage $\underline{K}_2$ of C_{3v} symmetry is assembled from altogether 10 $(OH)_6$ rings and 15 HQ *p*-phenylene linkers. Its relationship with the simple HQ supercube of $C_{60}(HQ)_3$ is particularly lucid since, idealized, it means a simple cage expansion through truncation of a single cube vertex located on the trigonal C_3 axis; compare Figures 3b and 3d. The cage $\underline{K}_2$ houses a single type $\underline{B}$ C_{70} guest molecule, which again has its long axis perpendicularly oriented with respect to the cage's C_3 axis. Type $\underline{B}$ C_{70} guest molecules encounter six FF and nine EF contacts with the encapsulating HQ molecules of their $\underline{K}_2$ cage: three FF with HQ($\underline{1}$), three FF with HQ($\underline{2}$), six EF with HQ($\underline{1}$), and three EF with HQ($\underline{3}$); see Figure 4b. The distances between the respective centers of gravity in this sequence are 6.93, 7.12, 8.60, and 8.79 Å. The coverage of C_{70} by the HQ ligands is thus seen to be of closely similar extent for both type $\underline{A}$ and $\underline{B}$ C_{70} fullerenes in their type $\underline{K}_1$ and $\underline{K}_2$ cavities, respectively.

The relatively small type $\underline{K}_3$ cages of C_{3v} symmetry are formed by four $(OH)_6$ rings and six HQ *p*-phenylene linkers. They take the shape of a trigonal pyramid with one type $\underline{R}_2$ $(OH)_6$ ring at the apex and three type $\underline{R}_3$ $(OH)_6$ rings defining the base of the pyramid. The *p*-phenylene connectors in the base derive from type $\underline{3}$ and the others from type $\underline{2}$ HQ molecules (Figure 3c). The shape of the $\underline{K}_3$ cage is, in fact, even roughly tetrahedral and has approximate T_d symmetry with opposite benzene rings juxtaposed in a face-to-face manner (Figure 4c). Difference Fourier syntheses tend to indicate that the tetrahedral cages $\underline{K}_3$ house a pair of benzene molecules essentially configurated according to a staggered face-to-face $(C_6H_6)_2$ sandwich of approximate symmetry D_{6d}, which, in turn, is sandwiched between two opposite HQ molecules of the $\underline{K}_3$ cage (Figure 4c). It is noted that the dimeric D_{6d} benzene sandwich is not a particularly favorable structure[5] but might possibly be stabilized by the sandwiching outer HQ pair of cage $\underline{K}_3$. The benzene sandwich model is orientationally disordered around the C_3 axis of the $\underline{K}_3$ cage, and the direct crystallographic evidence (room-temperature measurement!) appears insufficient to refer to this model as definitely proven, although its consideration in the refinements leads to a significantly improved F_o/F_c agreement. It should therefore be regarded as preliminary and requires further experimental backing. It, however, does meet the spatial requirements of the molecular partners involved, is in accord with NMR data, and helps to better the agreement between the observed and calculated density of the crystal. In addition, the $\underline{K}_3$ cage appears to provide extra space for some (probably favorable) lateral motion in the benzene sandwich. Finally, it cannot be rigorously excluded that the $\underline{K}_3$ cage contains certain amounts of quinone, which according to NMR measurements is present in the crystals in varying amounts; see the Experimental Section.

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[5] Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768.

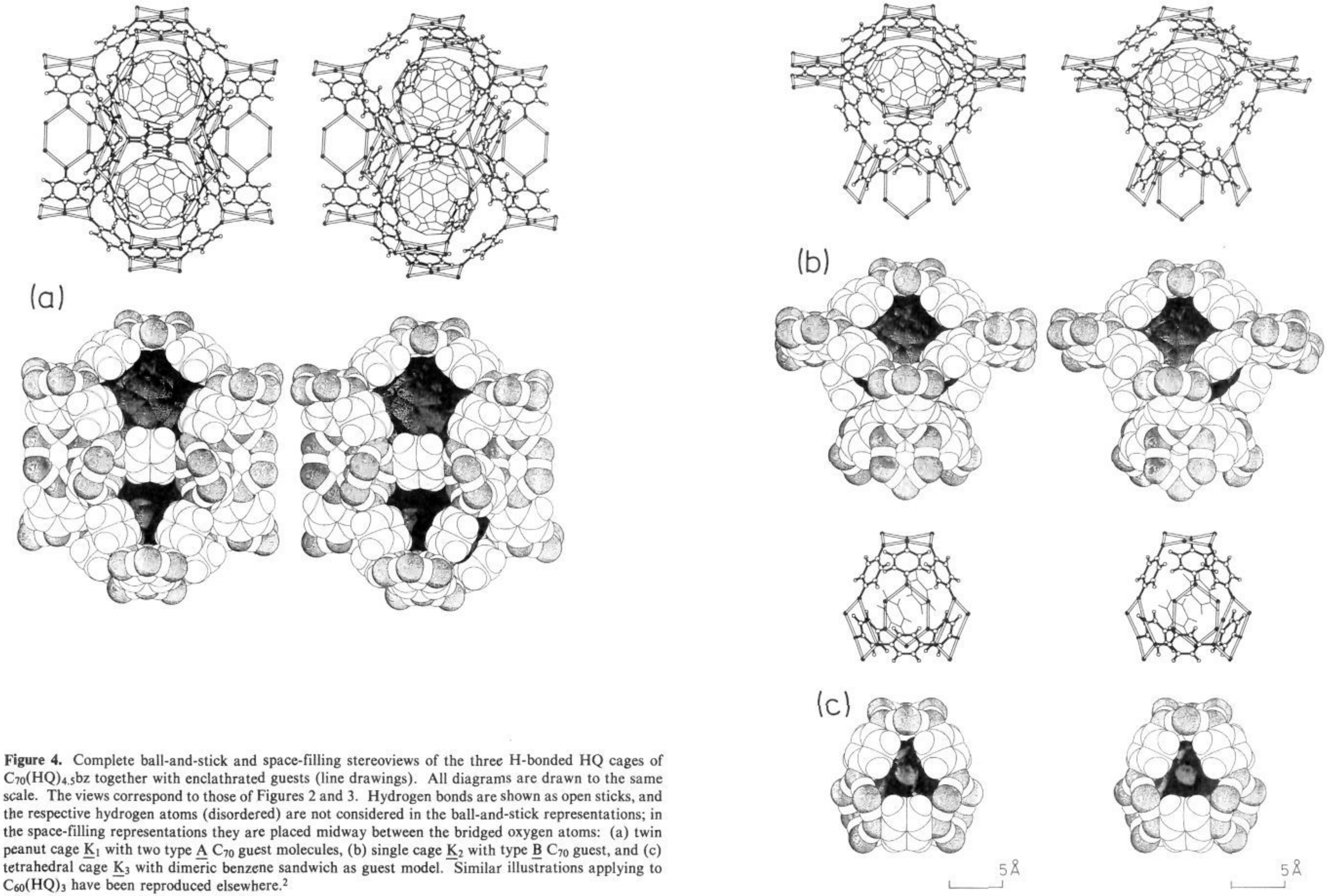

Figure 4. Complete ball-and-stick and space-filling stereoviews of the three H-bonded HQ cages of $C_{70}(HQ)_{4.5}bz$ together with enclathrated guests (line drawings). All diagrams are drawn to the same scale. The views correspond to those of Figures 2 and 3. Hydrogen bonds are shown as open sticks, and the respective hydrogen atoms (disordered) are not considered in the ball-and-stick representations; in the space-filling representations they are placed midway between the bridged oxygen atoms: (a) twin peanut cage $\underline{K}_1$ with two type $\underline{A}$ C_{70} guest molecules, (b) single cage $\underline{K}_2$ with type $\underline{B}$ C_{70} guest, and (c) tetrahedral cage $\underline{K}_3$ with dimeric benzene sandwich as guest model. Similar illustrations applying to $C_{60}(HQ)_3$ have been reproduced elsewhere.[2]

The tetrahedral cages $\underline{K}_3$ of the present complex are topologically related to the supertetrahedral building blocks of the pyrochlore network, which are assembled of four vertex-sharing MO_6 octahedra (general composition of oxidic pyrochlores, $M'_2M_2O_7$). These tetrahedral sets of four octahedra are joined via further vertex-sharing to build up a superdiamond network.[4] Transformation of the tetrahedral quartets of octahedra of pyrochlore into the cages $\underline{K}_3$ of our complex $C_{70}(HQ)_{4.5}bz$ simply requires replacement of the octahedral centers M by H-bonded $(OH)_6$ rings and of the bridging oxygen atoms by *p*-phenylene (see above). The structural comparison of our present new H-bonded HQ network and pyrochlore may be carried even further since every HQ $\underline{K}_3$ cage is linked to three other $\underline{K}_3$ cages (via type $\underline{R}_3$ $(OH)_6$ rings; Figure 2) to form large puckered "supercyclohexane" rings. The latter are fused into "superarsenic" sheets, which may of course be cut out of the diamond lattice. Suitable guest molecules provided, the creation of a cubic H-bonded HQ host network appears conceivable, consisting of $\underline{K}_3$-like HQ cages linked up to a superdiamond lattice. A supramolecular architecture of this kind would be entirely analogous to the 3D 6-connected pyrochlore network and would, in addition to the $\underline{K}_3$ cages, involve large superadamantane cavities of about 11-Å diameter, i.e., possibly the size of fullerenes larger than C_{70}.

Figures 1 and 2 give a pictorial impression about how the three different H-bonded HQ host cages are interwoven in the actual infinite crystal structure and thus also how the C_{70} guest molecules are disposed with respect to each other. We do not attempt a verbal description of these features. Suffice it to say that the three supramolecular H-bonded HQ cavities uncovered in this study have no precedent and add a new facet to the already rich inclusion chemistry of hydroquinone.

A brief remark concerning the direct C_{70}–C_{70} contact distances in the crystal of $C_{70}(HQ)_{4.5}bz$ is to be appended. As already mentioned, the C_{70}–C_{70} contact of the two type $\underline{A}$ molecules within the twin cage $\underline{K}_1$ is very close (center-of-gravity separation 10.10 Å). Neighboring type $\underline{A}$ and $\underline{B}$ C_{70} guest molecules may also assume close contact, provided a suitable mutual orientation is taken up (center-of-gravity separation 10.66 Å; long diameter of C_{70} about 11.2 Å, short diameter 10.0 Å). Type $\underline{B}$ C_{70} molecules have no possibility of close approach among each other since neighboring C_{70} $\underline{B}$ – $\underline{B}$ pairs have a center-of-gravity distance of 11.43 Å. Close C_{70}–C_{70} contacts may therefore be established only in infinite two-dimensional double sheets perpendicular to the trigonal *c* axis but not three-dimensionally throughout the whole crystal.

Conclusions

It may be stated that we have utilized the large C_{70} molecule as a vehicle, or template, to create a novel 3D H-bonded hydroquinone network with very large cavities. Imaginative supramolecular synthesis of host architectures capable of enclathrating very large guest species is an important, though still rather remote, goal of supramolecular chemistry in general. As an example, just consider the potential of enclathrating large biomolecules, be it only to expand the arsenal of biomacromolecular crystallization methodologies.[6] Returning to the HQ host, it will be interesting to observe in future experiments whether the supramolecular flexibility of HQ as emerging from the present study is versatile enough to adapt to still larger spherical[7] or even tubular[8] fullerenes as guests within still other H-bonded HQ host architectures.

Experimental Section

Crystallization. A 6:1 molar mixture of HQ and C_{70} (99.4%; Syncom BV, Groningen) was dissolved in hot benzene, and the solvent was slowly evaporated at room temperature. The resulting black shiny crystals took the shape of large hexagonal plates appearing clear brownish red in transmittent light. The high purity of C_{70} is crucial for producing good-quality crystals; initial crystallizations with 96% C_{70}, the rest being C_{60}, gave specimens yielding distinctly poorer diffraction patterns with less sharp reflections. Mass spectra showed high C_{70} and HQ crystal contents, and ^{1}H-NMR data revealed the presence of benzene with a HQ:benzene ratio of approximately 4.5:1. The NMR spectra also indicated the presence of variable amounts of quinone, but it remains unclear from our spectroscopic and X-ray analytical evidence whether this substance is indeed microscopically enclathrated or merely macroscopically (mechanically) occluded. (We thank G. Drabner and H. Schmickler for recording the spectra.) After about 2 months, the crystals of the C_{70} complex showed signs of decay (efflorescences of small slightly brownish needles). This and other properties support the conclusion that the C_{70}–HQ–benzene complex is less stable than $C_{60}(HQ)_3$. The present observation of C_{70} enclathration by HQ would appear to complicate C_{60} separation from higher fullerenes by the HQ inclusion crystallization envisaged earlier,[2] at least from benzene solution. A crystal of the C_{70} complex measuring ca. 0.4 × 0.4 × 0.2 mm^3 was used for the crystallographic measurements.

Crystal Data. Trigonal, space group $P\bar{3}m1$ (D^3_{3d}, No. 164), $Z = 4$ formula units of $C_{70}(HQ)_{4.5}bz$, i.e., $C_{103}H_{33}O_9$, per unit cell; $a = 17.102(5)$ Å, $c = 23.904(9)$ Å, $V = 6054.7$ Å^3; and $d_x = 1.551$ g cm^{-3}, $d_m = 1.54$ g cm^{-3}. A total of 7898 reflection intensities were measured at room temperature on a four-circle diffractometer (Mo Kα radiation $\lambda = 0.71069$ Å, $\theta_{max} = 25°$; average intensity drop over 6-days measuring time 5.4%); 3450 independent reflections with $I > 0$ were used for structure analysis, agreement index among equivalent intensities 0.021; 1709 reflections with $F_o > 3\sigma(F_o)$ were used for structure refinements; centrosymmetric space group $P\bar{3}m1$ was adopted throughout, supported by intensity statistics and structure analysis.

Structure Analysis. The crystal structure of $C_{70}(HQ)_{4.5}bz$ could not be solved routinely but only stepwise by a combination of packing considerations (comparison with $C_{60}(HQ)_3$ [2]), Patterson methods, direct phasing techniques, and difference Fourier syntheses. For example, the notion that the cell edge $c \simeq 24$ Å may be factored as 2(10) + 4 Å, whereas for $C_{60}(HQ)_3$ the hexagonal constant $c \simeq (10 + 4)$ Å,[2] hinted at a double cage in the C_{70} complex and an orthogonal orientation of the long C_{70} axis with respect to the trigonal crystal axis *c* (short diameter of C_{70} and diameter of $C_{60} \approx 10$ Å, thickness of puckered $(OH)_6$ ring ≈ 4 Å). The Patterson map could be exploited by interpreting the strongest maximum as the vector joining the midpoints of two neighboring type $\underline{A}$ and $\underline{B}$ C_{70} molecules, and C_{70} models constructed accordingly improved direct phasing calculations. Apart from a 2-fold orientational disorder of the hydroxyl H atoms, the HQ host molecules turned out ordered, while the C_{70} and benzene guest molecules are orientationally severely disordered.

Structure Refinement. The C and O atoms of the HQ molecules were refined anisotropically as usual (H atoms isotropic, hydroxyl H atoms with fixed positions). Type $\underline{A}$ and $\underline{B}$ C_{70} models centered on C_3 axes were constructed with a model building program, and six orientations for each were generated, which are related by crystallographic C_3 operations and reflections through virtual perpendicular mirror planes (individual orientations compliant with crystallographic mirror planes). The atoms of these disordered C_{70} models were refined anisotropically with their positional coordinates kept fixed, however (dampened block-diagonal least-squares calculations, atomic occupancies $^1/_6$). The *z* coordinates of the centers of gravity of both C_{70} molecules were optimized by stepwise *z* translations, structure factor calculations, and appropriate interpolation. A provisional disorder model of the two benzene molecules enclathrated in the tetrahedral cages $\underline{K}_3$ could be recognized from subsequent difference Fourier maps. Its refinement proceeded as for the C_{70} models (no H

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(6) Extremely hollow, alumosilicate-based molecular sieves have recently been prepared, which have potential for the inclusion of large biomolecules; see: Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

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Table I. Refined Atomic Coordinates and Temperature Parameters of $C_{70}(HQ)_{4.5}bz^{a}$

Hydroquinone Molecules

	x	*y*	*z*	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
C(11)	2025(4)	2*x*	3847(4)	95(5)	2*U*12	68(5)	43(3)	5(2)	2*U*13
C(12)	1143(5)	3677(5)	−13(3)	86(4)	2*U*12	83(5)	42(3)	8(2)	2*U*13
C(13)	760(5)	2929(6)	4347(3)	70(6)	2*U*12	58(6)	32(4)	1(3)	2*U*13
C(14)	1285(4)	2*x*	4516(3)	63(5)	79(6)	71(4)	44(5)	0(4)	1(4)
O(11)	2412(3)	2*x*	3515(3)	69(5)	81(6)	61(4)	48(5)	2(4)	8(4)
O(12)	912(3)	2*x*	4863(3)	80(6)	2*U*12	37(5)	31(4)	2(3)	2*U*13
H(12)	75(5)	384(5)	391(3)						
H(13)	14(5)	282(5)	454(3)						
$H_{ox}(11)$	307	519	342						
$H_{ox}(12)$	25	149	496						
C(21)	2*y*	5157(5)	1713(5)	125(6)	*U*11	84(5)	45(7)	26(3)	−*U*13
C(22)	525(7)	4564(6)	1966(3)	96(5)	*U*11	90(6)	36(6)	16(3)	−*U*13
C(23)	968(6)	4783(6)	2465(3)	2*U*12	89(7)	80(8)	47(5)	2*U*23	−11(4)
C(24)	4416(4)	1 − *x*	2726(4)	123(8)	83(7)	87(5)	62(6)	−20(6)	−18(5)
O(21)	4926(4)	1 − *x*	8787(3)	113(8)	67(6)	88(5)	50(6)	−22(6)	−6(5)
O(22)	4197(3)	1 − *x*	3244(3)	78(6)	*U*11	69(7)	33(8)	2(4)	−*U*13
H(22)	31(5)	393(5)	177(3)						
H(23)	103(5)	430(5)	270(3)						
$H_{ox}(21)$	443	468	905						
$H_{ox}(22)$	455	646	334						
C(31)	7187(6)	1194(6)	509(3)	104(5)	99(5)	107(4)	25(4)	19(4)	−4(4)
C(32)	7380(6)	1827(6)	929(3)	93(7)	83(7)	73(5)	31(6)	15(5)	0(5)
C(33)	7807(6)	1371(6)	88(3)	100(7)	83(6)	78(5)	26(6)	21(5)	1(5)
O(31)	6376(4)	382(4)	506(2)	108(7)	95(7)	72(5)	48(6)	12(5)	−2(5)
H(32)	700(5)	152(5)	126(3)						
H(33)	735(5)	86(5)	−27(3)						
$H_{ox}(31A)$	623	10	13						
$H_{ox}(31B)$	588	30	77						

C_{70} Model, Type A Molecule

	x	*y*	*z*		*x*	*y*	*z*
CA(1)	174	266	170	CA(20)	153	0	310
CA(2)	200	266	226	CA(21)	86	0	345
CA(3)	133	2*x*	261	CA(22)	40	−81	81
CA(4)	188	214	131	CA(23)	107	−81	116
CA(5)	239	214	241	CA(24)	157	−81	225
CA(6)	107	2*x*	310	CA(25)	132	−81	282
CA(7)	121	162	91	CA(26)	2	−81	350
CA(8)	228	162	146	CA(27)	−41	−162	91
CA(9)	253	162	201	CA(28)	65	−162	146
CA(10)	213	162	291	CA(29)	91	−162	201
CA(11)	147	162	325	CA(30)	51	−162	291
CA(12)	121	81	81	CA(31)	−15	−162	325
CA(13)	188	81	116	CA(32)	−26	−214	131
CA(14)	238	81	225	CA(33)	25	−214	241
CA(15)	213	81	282	CA(34)	−107	2*x*	310
CA(16)	82	81	350	CA(35)	−92	−266	170
CA(17)	41	0	66	CA(36)	−66	−266	226
CA(18)	179	0	137	CA(37)	−133	2*x*	261
CA(19)	205	0	194				

Benzene Model

	x	*y*	*z*		*x*	*y*	*z*
CBZ(1)	−1 + 2*y*	688	151	CBZ(4)	2 + 2*y*	−817	910
CBZ(2)	−1 + 2*y*	730	117	CBZ(5)	411	685	53
CBZ(3)	444	788	75				

[a] Coordinates of C and O atoms of HQ multiplied by 10^4, all other quantities by 10^3; atomic numbering of HQ atoms shown in Figure 1; H atoms bonded to C refined isotropically with common $U_{iso} = 0.13(1)$ Å^2; positions of H atoms bonded to O (H_{ox}) constructed and common $U_{iso} = 0.19(3)$ Å^2 refined; constructed independent coordinates (CA) of single orientation of the C_s symmetric C_{70} type A molecule listed only; coordinates for the type B C_{70} molecule obtainable via the transformation $x + {}^{2}/_{3}$, $y + {}^{1}/_{3}$, and $z + 0.169$; optimized centers-of-gravity of type A and B C_{70} molecules at 0, $\bar{0}$, 0.2112 and ${}^{2}/_{3}$, ${}^{1}/_{3}$, 0.3797, respectively; benzene model (CBZ) derived from difference Fourier maps; refined anisotropic parameters of C_{70} and bz models not given since they are physically meaningless due to disorder.

atoms considered). Apart from some dimensional idealizations, the essential features of the dimeric benzene D_{6d} sandwich model as shown in the figures are in accord with the crystallographic findings. The *R* value after conclusion of the refinements was 0.104 (unit weights, goodness-of-fit 3.11). Relevant atomic positional and thermal motion parameters are collected in Table I.