130. 3:1 Molecular Complex of Hydroquinone and C_{60}

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The preparation of a 3:1 complex of hydroquinone (HQ) and C_{60}, $(HQ)_3C_{60}$, is reported and its X-ray crystal structure described. The HQ host builds up a single H-bonded super-polonium network with super-cubes as building blocks, which accommodate the large C_{60} guest molecules. The enclathration of C_{60} is rather tight (high density of the complex) owing, in part, to favorable charge-transfer host-guest interactions (π-donor-acceptor complex). Nonetheless, the C_{60} molecules are orientationally disordered, and no individual bond lengths could be measured. In contrast, the HQ host network is essentially ordered and well-defined with normal intramolecular geometry. No appreciable (powder) conductivity could be observed for $(HQ)_3C_{60}$, yet ESR spectra of single crystals showed interesting narrow signals.

Introduction. – In the rhombohedral crystals of space group $R\bar{3}$ the β-form of hydroquinone (HQ) formes open-meshed three-dimensional networks with 'super-polonium' structure, which are held together by O(H)O H-bonds. Building blocks of these networks are large 'super-cube' cages with spaceous central cavities, which are largely filled by symmetric interpenetration of a second (translationally equivalent) network. The corners of the super-cubes are made up of H-bonded $(OH)_6$ rings, from which six *p*-phenylene groups emanate in distorted octahedral fashion. The *p*-phenylene groups represent the super-cube edges and act as covalent bridges between the $(OH)_6$ corners. The super-cubes are trigonally compressed along the space diagonal running perpendicular to the mean plane of the $(OH)_6$ hexagons. Despite the twofold interpenetration, the β-HQ architecture is not very tightly packed (relatively low density of 1.256 gcm^{-3}) and still involves appreciable cavities capable of accommodating small guest molecules such as H_2S, CH_3OH, or CH_3CN [1].

Closer contemplation suggests that the super-cube cavities of a *single* β-HQ network offer good geometrical prerequisites for inclusion of an icosahedral C_{60} molecule, since the edge length of the super-cubes and the diameter of the C_{60} ball almost coincide (*ca.* 10 Å). Such a supramolecular host-guest complex between HQ and C_{60} would have 3:1 stoichiometry. Furthermore, it may be expected that complex formation will in substantial measure also be supported by the π-electron-donating properties of HQ, as C_{60} has proved to be an unusually strong electron acceptor [2].

Based on these considerations, we could indeed prepare a 3:1 complex between HQ and C_{60} by simple stoichiometric mixing of the components in solution and subsequent crystallization. We could then show by X-ray crystallography that the complex $(HQ)_3C_{60}$ builds up the expected super-polonium host-guest architecture in the crystal. Our interest in this $(HQ)_3C_{60}$ complex was spurred by the possibility to measure structural data on a C_{60} molecule perturbed only intermolecularly without involvement of heavy atoms, as contrasted to recent X-ray analyses of two more or less covalent heavy-atom derivatives [3]. Furthermore, electric conductivity might be envisaged for $(HQ)_3C_{60}$, since analogies may obviously be drawn with the highly conductive (and superconductive) potassium salt K_3C_{60} [4]. However, it was found that the C_{60} molecules are orientationally disordered in $(HQ)_3C_{60}$, and preliminary conductivity measurements gave low σ values. On the other hand, interesting narrow signals could be detected in ESR spectra.

Experimental. – Pure C_{60}, now available in macroscopic quantities due to the seminal work of *Krätschmer et al.* [5], and hydroquinone (HQ) of molar ratio 1:3 were dissolved in hot benzene, and the solvent gradually evaporated without taking any special precautions. After several days, black dendritic crystals began to appear, which eventually grew to a length of up to 7 mm. Essentially no other crystalline material precipitated, and since the air-stable dendrites appeared homogeneous, this indicated formation of the complex $(HQ)_3C_{60}$. The individual, rather large black single crystals, making up the branches of the dendrites, display shiny faces of metallic luster and take the shape of sharp-edged, more or less complete rhombohedra, particularly beautiful at the tips of the dendritic arms. In transmittent light, the brittle crystals appear dark brownish red. They proved to be of excellent single-crystalline quality and gave a well-defined, sharp diffraction pattern extending beyond $\Theta_{Mo} = 30°$. Damage on exposure to X-rays (Mo radiation) is small, if at all perceptible. It is noted that in initial exploratory crystallization experiments with a 5:1 C_{60}/C_{70} mixture1) replacing pure C_{60} large, black dendrites could also be produced from benzene and toluene solns. with stoichiometric quantities of HQ. This material was highly crystalline, yet not single-crystalline and unsuitable for further X-ray analytical work. According to ^{13}C-NMR and MS evidence, it consisted largely of the $(HQ)_3C_{60}$ complex suggesting a simple method of separating C_{60} from C_{70} (and possibly also from higher fullerenes). Although the crystallizations applying the C_{60}/C_{70} mixture appeared rather 'dirty' and produced only heavily intergrown specimen of the HQ complex, they provided encouragement enough to proceed to experimenting with pure C_{60}. All work reported further on refers to $(HQ)_3C_{60}$ crystals grown with the help of pure C_{60} under very 'clean' conditions.

A well-developed crystal measuring *ca.* 0.4 × 0.5 × 0.6 mm^3 was cut off from a dendritic branch and used for the subsequent crystallographic measurements.

Crystal Data. Rhombohedral, space group $R\bar{3}m$ (D^5_{3d}, No. 166), $Z = 3$ formula units $(HQ)_3C_{60}$, *i.e.* $C_{78}H_{18}O_6$, per hexagonal unit cell; hexagonal cell constants, $a = 16.215(2)$, $c = 13.846(2)$ Å, $V = 3152.7$ Å^3 (rhombohedral cell constants, $a' = 10.438(2)$ Å, $\alpha = 101.92(2)°$; $a' = 1/3\,(c^2 + 3a^2)^{1/2}$, $\sin(\alpha/2) = a/(2a')$); $d_x = 1.660$, $d_m = 1.65$ gcm^{-3} (flotation, aq. KI soln.); temp. 295 K. The average crystallographic symmetries of HQ and C_{60} are C_{2h} and D_{3d}, respectively, in the complex (*Fig. 1*). A total of 2432 reflection intensities were measured on a *CAD-4* diffractometer (MoK_α radiation, $\lambda = 0.71069$ Å, $\Theta_{max} = 30°$; average intensity drop of two monitor reflections 1.2% over total measuring time of 57 h). The measured data set comprised more than 1/3 of reciprocal space, *i.e.* for every reflection at least one equivalent reflection was measured in order to probe the *Laue* symmetry of the crystal. This symmetry resulted as $\bar{3}m$ (D_{3d}) with a high degree of reliability, as indicated by an agreement index of 0.010 among the equivalent intensities. After averaging, 1126 unique reflection intensities remained, which were used for structure analysis. Of these, 958 reflections with $F_o > 4\sigma(F_o)$ were considered in the subsequent refinements. Statistical tests, direct methods, and general structural-chemical considerations strongly indicated the average centrosymmetric space-group symmetry $R\bar{3}m$, which was finally adopted in all crystallographic calculations. A space-group symmetry diagram is shown in *Fig. 1*.

Structure Analysis. E-maps based on direct method phases showed the HQ atoms as strong maxima at the expected positions around a C_{2h} site. The other prominent peaks were only about half as intense and were located within narrow limits on a sphere of radius 3.51 Å centered on a D_{3d} site. These latter peaks are, thus, obviously associated with the C_{60} molecule, yet could not be assigned to individual atoms corresponding to a sensible C_{60} geometry. Attempts to interpret these C_{60} peaks in terms of averaged atomic positions resulting from a superposition of several molecular orientations were only partly successful (see below). Inspection of sharpened *Patterson* and later electron density (F) and difference density (ΔF) maps did not change this picture; neither did trial analyses applying the non-centrosymmetric space groups $R3m$, $R32$, or the centrosymmetric choice $R\bar{3}$ with lower *Laue* symmetry. The electron density of the C_{60} molecule appeared to be distributed on a spherical shell of radius 3.5 Å with relatively shallow maxima smeared out tangentially over the sphere. It seems clear from these observations that the C_{60} molecules are highly disordered in the present hydroquinone complex. The disorder is

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1) I thank *W. Krätschmer*, Heidelberg, for a generous gift of the C_{60}/C_{70} mixture.

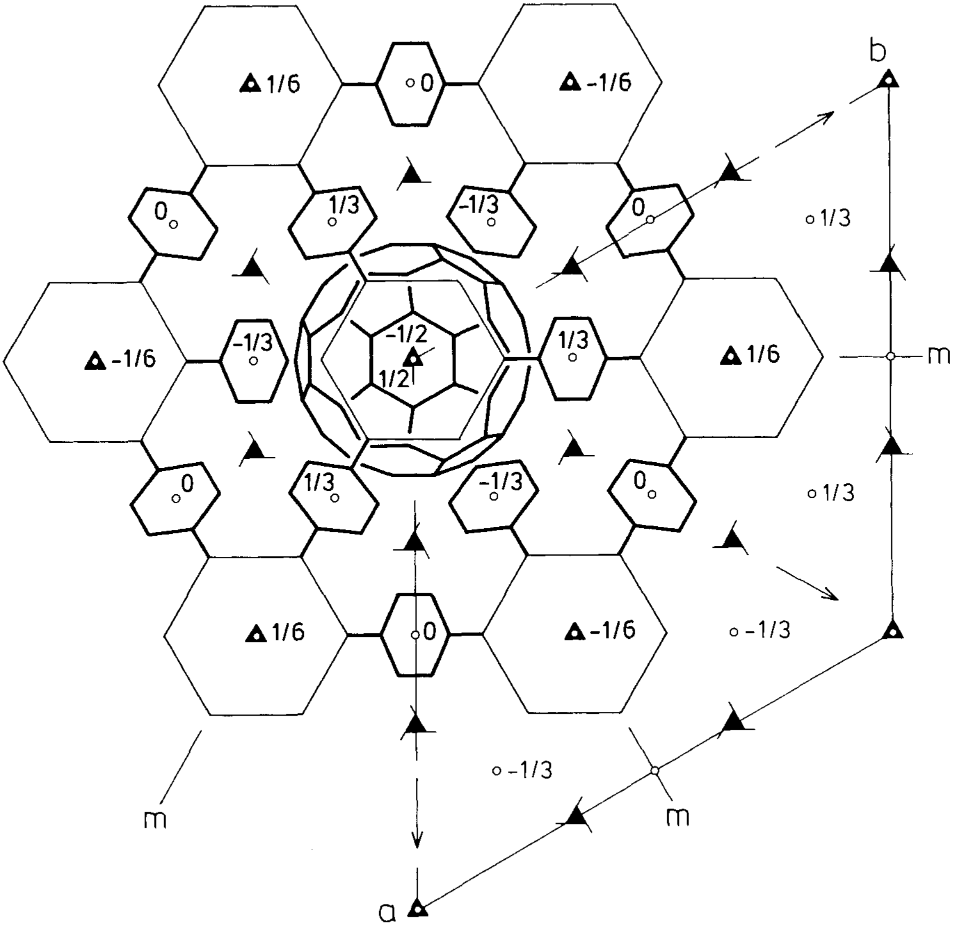

Fig. 1. *Space-group* ($R\bar{3}m$) *symmetry diagram of* $(HQ)_3C_{60}$, *projected along the hexagonal* c *axis*. The elements of one super-cube of the HQ host network are drawn, together with the enclathrated C_{60} molecule located on the origin. The atomic positions of C_{60} are constructed (see Text). The large hexagons (thin lines) represent the H-bonded $(OH)_6$ rings forming the corners of the super-cube, which are bridged by the HQ phenylene groups (super-cube edges). Two $(OH)_6$ rings in the center of the diagram are superimposed along the hexagonal c axis representing a space-diagonal of the super-cube. The elevations of the HQ and $(OH)_6$ centers are given in units of c. Only a selection of symmetry elements is shown in the diagram, in particular point symmetries.

purely orientationally as expected for the C_{60} spheres being tightly enclathrated in the super-cube cavities of the HQ host network. Whether this disorder is dynamic or static, remains to be investigated. In the first case, the C_{60} molecules would actually switch between different orientations at room temperature, in the latter different orientations would be statistically distributed over the unit cells, but would not change with time. In view of the tight packing in $(HQ)_3C_{60}$ (see *Discussion*), we are inclined to believe in the static disorder variant. More respective insight clearly requires low-temperature measurements, which are in progress. The present disorder analysis and the C_{60} electron-density model adopted in the refinements should, therefore, be considered as preliminary. However, apart from the orientational C_{60} disorder, our present X-ray analysis establishes beyond doubt that $(HQ)_3C_{60}$ has indeed the expected structure. The crystallographically well-defined HQ host architecture consists of a single super-polonium network with one C_{60} guest molecule confined in every super-cube cavity.

Structure Refinement. The C- and O-atoms of HQ were refined anisotropically as usual and assumed rather precise positional parameters and low-temperature motion (*Table*). Even the two independent hydrogen atoms could be partially refined isotropically (*Table*). As a consequence of the crystallographic mirror planes running through the HQ O-atoms (and perpendicular to the aromatic ring), the phenolic H-atoms are twofold orientationally disordered (*Fig. 2*). The approximately spherical-shell shaped electron density of the C_{60} molecule was modeled in the refinements by considering the eight most prominent E-map maxima (as resulting from direct methods), which were located on a sphere with radius 3.5 Å around a D_{3d} site, and which did not approach each other by less than 1.0 Å. Five of these maxima were located on mirror planes, three in general (asymmetric) positions (*Table*).

Table. *Refined Atomic Coordinates* (×10⁴, hydrogen ×10³) *and Temperature Parameters* (×10³) *of* $(HQ)_3C_{60}$ (estimated standard deviations in parentheses). Anisotropic temperature factor expression, $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^* + \ldots)]$. The positional parameters of the twofold disordered (half-weighted) atom H_{ox} were constructed and fixed, since, if refined, the HOC angle assumed unrealistically large values. The C-positions of the (orientationally disordered) C_{60} model, designated 'CS', originate from an E map based on direct method phases (see Text). CS(6) assumes extremely large thermal coefficients U_{11}, U_{22}, U_{12}, and the vibrational tensor is not positive definite. However, omission of CS(6) from the refinement causes the R value to increase markedly from 0.198 to 0.236, since U_{33} is small.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hydroquinone (HQ)									
C(1)	1310(2)	-1310(2)	4031(4)	25(2)	25(2)	29(3)	1(1)	-1(1)	11(2)
C(2)	2589(3)	3688(3)	2986(3)	19(2)	41(3)	38(2)	-8(2)	1(2)	16(2)
O	2374(2)	-2374(2)	1942(4)	54(3)	54(3)	47(3)	-5(1)	5(1)	31(3)
H(2)	266(3)	277(3)	390(3)	29(11)					
H_{ox}	122	155	492	84(46)					
C_{60} *Model*									
CS(1)	5748(4)	-5748(4)	5065(7)	139(10)	139(10)	51(5)	-24(2)	24(2)	113(11)
CS(2)	-2649(5)	2649(5)	5461(9)	202(15)	202(15)	48(7)	21(3)	-21(3)	170(16)
CS(3)	-2074(3)	2074(3)	3260(12)	124(12)	124(12)	104(12)	-5(3)	5(3)	113(13)
CS(4)	-2305(5)	2305(5)	4808(10)	132(10)	132(10)	68(7)	23(3)	-23(3)	102(11)
CS(5)	4909(8)	3647(13)	4465(13)	66(7)	180(14)	165(16)	-89(13)	9(8)	71(8)
CS(6)	-3098(18)	3098(18)	5728(11)	870(87)	870(87)	31(6)	64(9)	-64(9)	672(88)
CS(7)	4452(9)	2891(18)	4165(10)	88(8)	504(34)	79(7)	66(15)	40(7)	184(15)
CS(8)	4323(9)	1428(11)	3035(12)	68(7)	98(9)	145(12)	12(10)	-17(7)	-5(6)

Anisotropic refinement as C-atoms (in addition to the HQ parameters) eventually led to an R value of 0.198 ($R_w = 0.210$, $w = 1/\sigma^2(F_o)$; $R = 0.604$ without considering the C_{60} refinement model). Expectedly, the anisotropic temperature factor tensors of the C_{60} model positions roughly take the shape of extended flat discs with the small principal axis pointing radially. Exclusion of inner reflections did not lead to much lowering of the rather high R values. This reflects deficiencies of the adopted C_{60} disorder model and shows the high scattering contributions of C_{60} to both low- and high-order reflections. The origin of this unusual situation is probably to be sought in the fact that the special disorder behavior of C_{60} does not lead to a complete randomization of its electron density, yet only to a spreading over a well-defined and relatively narrow spherical shell. It is noted further that a refinement involving a superposition disorder model for C_{60} converged to $R = 0.303$ ($R_w = 0.324$). This model consisted of a 1:1 superposition of the two different C_{60} orientations (relative to the HQ molecules) allowed crystallographically under D_{3d} symmetry. The atomic positions of both (half-weighted) C_{60} orientations (differing by a 60° rotation around the hexagonal c axis) were constructed applying the experimental sphere radius of 3.5 Å, and subsequently refined anisotropically together with the standard anisotropic HQ parameters. (One of the two superimposed, constructed D_{3d} models of C_{60} was used to prepare the illustrations shown in *Figs. 1* and *3–5*.) Summing up, it appears that the C_{60} disorder model derived from direct methods (and also, to a lesser extent, the constructed superposition model) is rather sensible in view of the R value soaring from *ca.* 0.20 to 0.60 on omission of the modeled C_{60} structure factor contributions. On the other hand, this C_{60} disorder model is not perfect, since otherwise a lower R value than 0.198 should have been attained in view of the presumably good quality of the measured X-ray intensities. The refined positional and temperature parameters are collected in the *Table*. *Figs. 1–5* show a space-group symmetry diagram, thermal ellipsoids and geometry data of hydroquinone, and various stereo views highlighting the supramolecular architecture of the present super-polonium inclusion compound $(HQ)_3C_{60}$. All results reported refer to the refinement leading to $R = 0.198$ (C_{60} model from direct methods).

Discussion. – *Structure.* The orientational disorder of the C_{60} molecules in the present complex $(HQ)_3C_{60}$ precludes the measurement of individual bond lengths. However, the radius of C_{60} (average distance of refined atomic model positions from molecular center on D_{3d} site) could be reliably established as 3.5 Å in agreement with previous structural work [3] [5]. In *Figs. 1* and *3–5*, one of the two orientations (relative to HQ) possible under D_{3d} site symmetry in space group $R\bar{3}m$ was, therefore, constructed using the experimental radius of C_{60}.

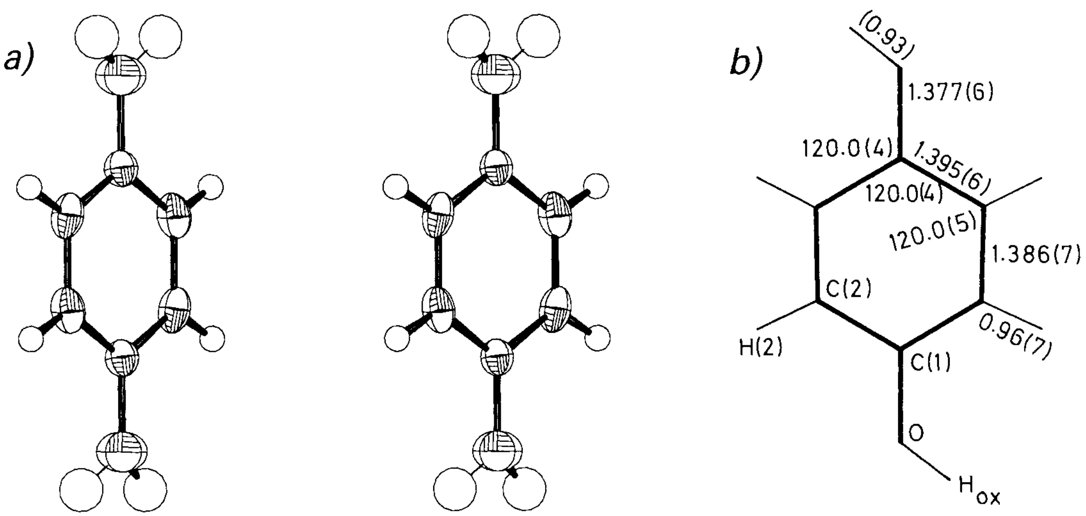

Fig. 2. *Structure of hydroquinone* (HQ, symmetry C_{2h}) *in the complex* $(HQ)_3C_{60}$. *a*) Stereoview with vibrational ellipsoids (50% probability); U_{iso} of H-atoms halved, position of H_{ox} constructed. Two excess H_{ox}-atoms are shown (thin O–H bonds) to illustrate the twofold disorder. *b*) Atomic numbering, bond lengths [Å], and bond angles [°].

In contrast to the disordered spherical guest molecules C_{60}, the hydroquinone (HQ) host molecules are ordered (except for the two-fold orientational disorder of the OH groups) and structurally well defined, despite the relatively high R value after refinement. *Fig. 2* shows the rather unexceptional geometry data of the essentially planar molecule, which compare well with HQ structures from other sources (except for small exocyclic angular distortions at C(1) in free HQ, which are averaged out in the present complex by the orientational OH disorder across the crystallographic mirror planes on which the HQ molecules reside). The tight complexation with C_{60}, thus, does not lead to perceptible structural distortions of HQ. The temperature motion of HQ is relatively low in $(HQ)_3C_{60}$ and shape and orientation of the vibrational ellipsoids (*Fig. 2*) comply with the way the HQ molecules are sandwiched by C_{60} guest molecules in the crystal of the complex (see below).

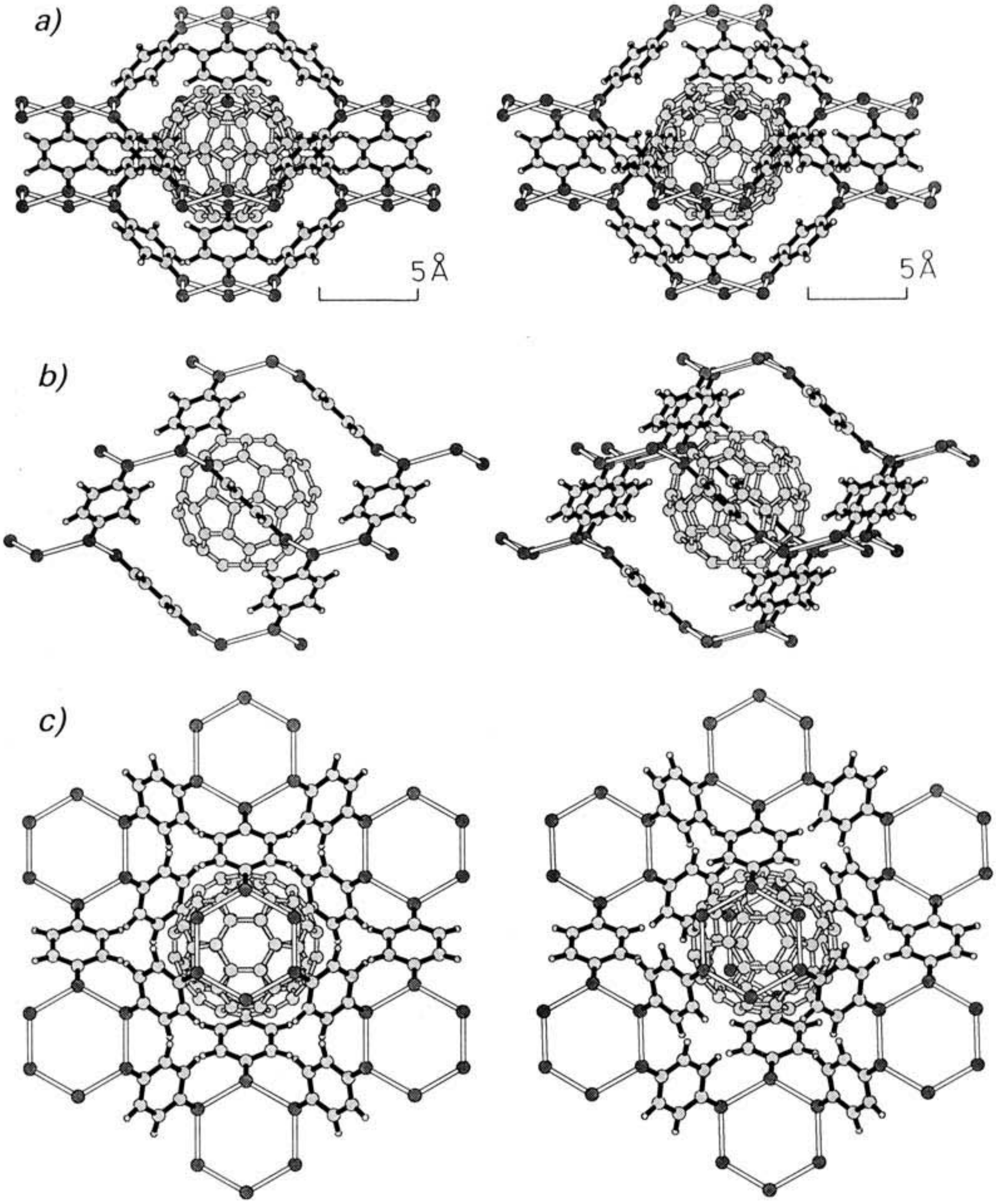

Fig. 3. *Ball-and-stick stereoviews of the super-polonium architecture of (HQ)$_3$C$_{60}$.* One H-bonded HQ super-cube cut out of the three-dimensional network is shown, together with the enclathrated C_{60} molecule. The representation of C_{60} is based on constructed atomic coordinates (see Text). The bridging H-atoms of the $(OH)_6$ rings are omitted, and the O(H)O bridges are drawn as white bonds; note the pronounced chair-like puckering of the $(OH)_6$ rings. Consider also the two kinds of HQ/C_{60} interactions: six polar FTF and six equatorial ETF contacts. *a*) View perpendicular to hexagonal *c* axis (vertical) and a twofold axis (horizontal); a mirror plane runs vertical (orthogonal to twofold axis and containing *c* axis). *b*) View along a twofold axis, *c* axis vertical. *c*) View along hexagonal *c* axis (compare to *Fig. 1*). The definition of the views holds strictly for the left-hand members of the stereopairs.

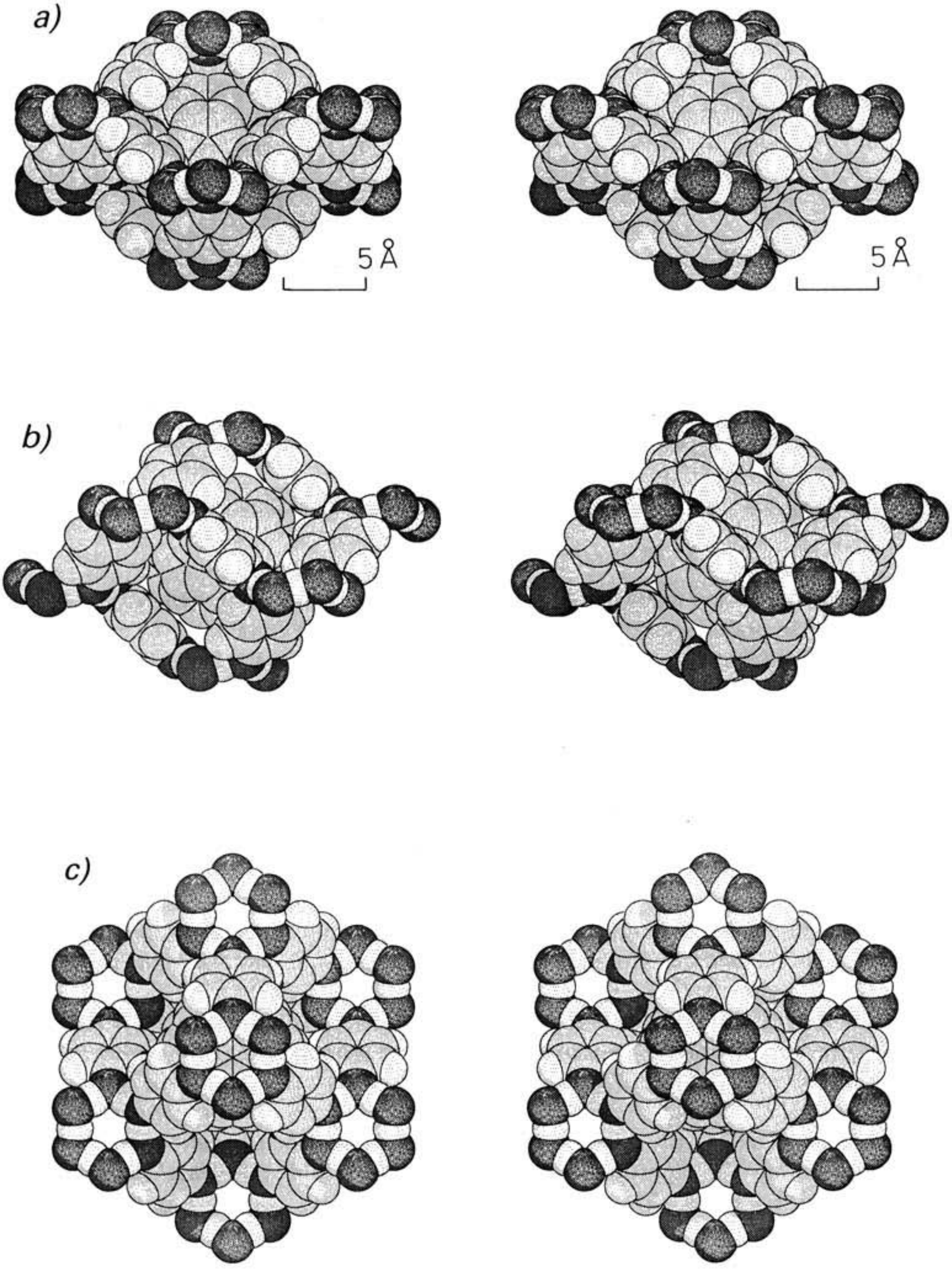

Fig. 4. *Space-filling stereoviews of the super-polonium architecture of* $(HQ)_3C_{60}$. The super-cube units shown and the viewing directions correspond to the analogous ball-and-stick representations of *Fig. 3* (see respective legend). For convenient drawing, the bridging H-atoms of the chair-like $(OH)_6$ rings are placed symmetrically on twofold axes perpendicular to the H-bonds.

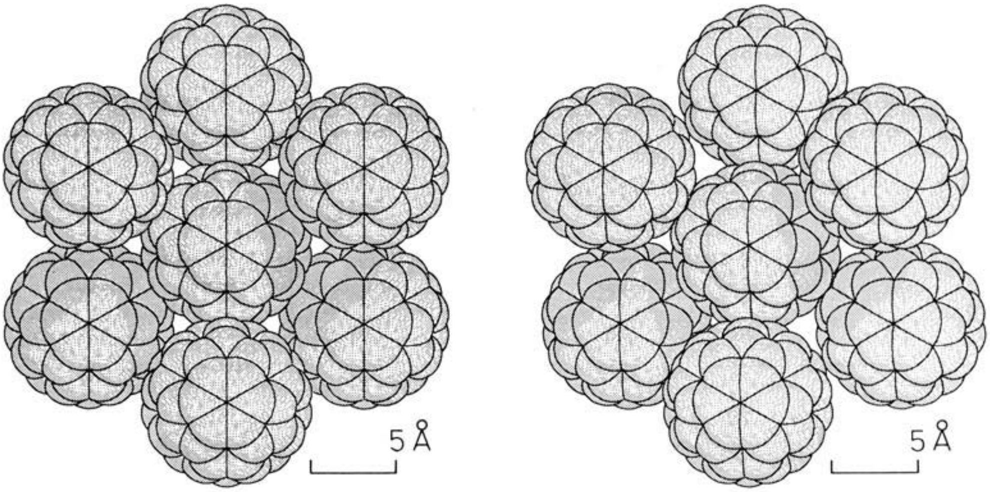

Fig. 5. *Space-filling stereoview* (along hexagonal *c* axis) *of the distorted octahedral self-coordination of* C_{60} *in the complex* $(HQ)_3C_{60}$

The structural characteristics of the H-bonded super-polonium architecture of the HQ host in the present complex $(HQ)_3C_{60}$ may favorably be illuminated by comparison with the analogous structure of the β-form of hydroquinone (β-HQ) itself. The hexagonal cell edges $a = 16.613$, $c = 10.949$ Å of β-HQ [6] (c edge doubled to account for twofold interpenetration; rhombohedral cell edge, *i.e.* edge length of the super-cubes of β-HQ, $a' = 10.262$ Å) deviate significantly from those of $(HQ)_3C_{60}$, $a = 16.215$, $c = 13.846$ Å ($a' = 10.438$ Å), in particular the hexagonal edge c. The same observation applies to the usual β-HQ inclusion compounds with double host interpenetration [1]. The ensuing considerable trigonal elongation of the HQ super-cubes in $(HQ)_3C_{60}$ as compared to β-HQ itself may essentially be traced to the geometry of the H-bonded $(OH)_6$ rings, which are highly puckered in the present complex (*Fig. 3a, b*) yet almost flat in the doubly interpenetrating β-HQ structures. Through the puckering, the large $(OH)_6$ rings in $(HQ)_3C_{60}$ assume a chair conformation, which has crystallographic D_{3d} symmetry like the chair form of cyclohexane. The O(H)O(H)O angles and O(H)O(H)O(H)O dihedral angles have magnitudes of 112.9 and 50.5°, respectively, as compared to 111.4 and 54.9° applying for cyclohexane [7]. So, to put things in perspective, the $(OH)_6$ ring pucker in $(HQ)_3C_{60}$ is very appreciable (*Fig. 3a, b*) and only slightly smaller than in the cyclohexane chair. The O(H)O distance of the H-bonds in $(HQ)_3C_{60}$ is 2.799 (5) Å, slightly stretched in comparison to β-HQ (2.678 Å). The H-bonded super-cubes are trigonally compressed, as characterized by the appropriate ratio of the two different space diagonals of $3c(12a^2 + c^2)^{-1/2} = 0.718$. (This trigonal compression is also evident from the fact that the rhombohedral angle, $\alpha = 101.92°$, is larger than 90°; see *Experimental.*) The respective compression of free β-HQ with its relatively short cell edge c is of course more pronounced, the ratio of the diagonals being 0.561 (rhombohedral angle, $\alpha = 108.1°$). The elongation of the super-cubes in $(HQ)_3C_{60}$ relative to those of β-HQ effected by the $(OH)_6$ chair-like pucker lead to a 20.5% increase of the cell volume (hexagonal values, 3152.7 and 2617.0 Å^3, respectively). Evidently, the enclathration of the large C_{60} spheres by a single HQ super-polonium network requires a considerable distortion, that is an enlargement, of the H-bonded super-cubes as compared to β-HQ, which enclathrates a second equivalent, less space-demanding network. (β-HQ is, thus, a self-inclusion compound.) The conclusion follows quite naturally that the C_{60} molecules should be pretty tightly locked up in the 'strained' supercubes, and this is rather dramatically expressed through the comparatively high density of $(HQ)_3C_{60}$, 1.660 gcm^{-3}. This value is almost the same as that of C_{60} itself (1.678 gcm^{-3} [5]), in contrast to the low density, 1.256 gcm^{-3}, of β-HQ (the densities of the α- and γ-forms of free HQ being also relatively low, 1.362 and 1.379 gcm^{-3}, respectively) [1b]. These observations support our assumption that the orientational disorder of C_{60} in $(HQ)_3C_{60}$ is static and hint at unusually strong and favorable host-guest interactions (see below). Furthermore, the C_{60}/C_{70} separation phenomena, occurring in our initial complex crystallizations applying a 5:1 C_{60}/C_{70} mixture rather than pure C_{60} (see *Experimental*), find their ready explanation by the same line of arguments, since the HQ super-cubes, already severely stretched in $(HQ)_3C_{60}$, will hardly be inclined to comply with the still larger space demands of C_{70}, *i.e.* will not expand even further.

In keeping with the lower space-group symmetry ($R\bar{3}$ *vs.* $R\bar{3}m$), the super-cubes of β-HQ have only S_6 symmetry as compared to D_{3d} for our complex $(HQ)_3C_{60}$. Similarly, the HQ molecules in β-HQ are only C_i-symmetric but have the higher C_{2h} symmetry in the complex. Thus in β-HQ a 'tilt' of the benzene rings (rotation around the long intramolecular O–O axis of HQ) is symmetry-allowed and actually observed to occur to a significant extent [1]. The origin of this tilt seems to be due to steric demands, which have to be satisfied for accomodation of the second interpenetrating super-polonium network. The mirror planes in $(HQ)_3C_{60}$ with its single super-polonium host lattice preclude the tilt of the HQ host molecules, which here is actually not necessary but would rather impair the good-to-face contacts of HQ and C_{60} (*Figs. 1, 3,* and *4*).

The present supramolecular complex $(HQ)_3C_{60}$ is the first example of a β-HQ-type inclusion compound with a *single*, extremely hollow super-polonium host network. All other HQ inclusion compounds of this class known so far have a *double* super-polonium host architecture with comparatively small cavities and, thus, also small molecular guests [1]. The 'giant' C_{60} molecules enforcing the single host network in $(HQ)_3C_{60}$ have a molecular mass 2.2 times larger than that of three HQ molecules, and occupy 50% of the crystal volume! $(HQ)_3C_{60}$ represents one of the rare inclusion compounds with more guest than host material, and to the best of our knowledge may be the most extreme case in this sense uncovered so far. One is irresistibly reminded to a tropical snake devouring a prey of disproportionately larger cross-section than that of her normally slim body! Clearly, in our structural-chemical context the question arises as to whether the labels 'host' and 'guest' should be reversed in cases such extreme as $(HQ)_3C_{60}$, and there would indeed be some reason to do so, since the intermolecular C_{60}/C_{60} interactions are rather favorable. Adopting indeed C_{60} as the host, its supramolecular architecture is also that of a super-polonium structure with exactly the same dimensions as that spanned by the H-bonded HQ molecules. We will come back to this characterization further below. Concluding the supramolecular comparison of β-HQ and $(HQ)_3C_{60}$, it may be stated that both have a double super-polonium architecture, but whereas the two symmetrically interpenetrating networks are (translationally) equivalent both chemically and geometrically in β-HQ, they do so only geometrically in $(HQ)_3C_{60}$. The latter complex represents a 'mixed' double super-polonium structure with one H-bonded network made up of the HQ molecules, and the second interpenetrating one formed by the C_{60} molecules *via π–π van-der-Waals* contacts.

The most interesting aspect to look for in the complex $(HQ)_3C_{60}$ concerns the supramolecular host-guest interactions. Special attention is also to be paid to the C_{60}/C_{60} contacts, which are still present in the complex (see concluding paragraph of this section). *Figs. 1, 3, 4,* and *5*, respectively, serve to illustrate the following discussion. The best packing mode of the free spherical C_{60} molecule itself appears to be a closest-packed arrangement, either cubic or hexagonal, but less symmetric packings seem to be energetically only little worse; C_{60}/C_{60} contact distances of 10.02, 10.04, and 10.113 Å have been reported [5] [8]. In the closest-packed arrangements, C_{60} has twelve equivalent contact neighbors. After entering the HQ super-cubes in $(HQ)_3C_{60}$, the C_{60} molecules retain six C_{60}/C_{60} contacts at a somewhat extended distance of 10.438 Å (= rhombohedral cell edge length a', see above). Given the 7.0-Å diameter of the C_{60} C-skeleton, this leads to a distance of 3.4 Å between the two contacting C-spheres, comparable to the interplanar stacking distance in graphite (3.35 Å). It is conceivable to think of small outward 'bulges' of the C_{60} spheres in contact direction in order to reduce the C_{60}/C_{60} contact distances, but this cannot be reliably deduced from the present measurements due to the orientational disorder of the C_{60} molecules. Six C_{60}/C_{60} contacts are given up on complex formation and are replaced by six 'polar' face-to-face (FTF) and six 'equatorial' edge-to-face (ETF) contacts with HQ, such that each encapsulated C_{60} molecule touches altogether 18 neighboring molecules (*Figs. 1* and *3–5*). The descriptors 'polar' and 'equatorial' refer to the globular C_{60} molecule with north and south poles located on the crystallographic hexagonal axis. *Fig. 1* (and similarly *Figs. 3* and *4*) shows clearly that the two inner rings of (each 3) 'polar' HQ molecules around the encapsulated C_{60} molecule have FTF contact with C_{60} extending over areas of the northern and southern hemispheres. The six 'equatorial' HQ molecules of the outer girdle experience ETF contacts undulating around the equator of the C_{60} molecule.

The distance between the C_{60} centers and the polar FTF-oriented HQ moleculer centers amounts to $1/6(3a^2 + 4c^2)^{1/2} = 6.574$ Å (*Fig. 1*), which leads to a distance of 3.1 Å between the HQ plane and the C-surface of C_{60} applying a radius of 3.5 Å for the latter. It is interesting to note that the interplanar stacking distance in the 1:1 charge-transfer (CT) complex of HQ and quinone (quinhydrone) is also 3.1 Å [9]. This observation suggests that the nature of the FTF interaction of HQ and C_{60} in the present complex $(HQ)_3C_{60}$ is also CT-like, in line with the high electronegativity of C_{60} [4] and the π-donor properties of HQ. Supporting evidence in terms of a CT interaction between HQ and C_{60} may be derived from the deep color and metallic luster of the complex crystals (see *Experimental*). Futile efforts to prepare an inclusion compound of C_{60} with 2,6-dimethylideneadamantane-1,3,5,7-tetracarboxylic acid as host may possibly also be viewed in this sense: this tetrahedral tetracarboxylic acid has recently been shown to possess a very high propensity for diamond-like inclusion of foreign guest molecules [10], and a H-bonded, double super-diamond host architecture appears geometrically well-suited for accomodation of C_{60} guest molecules with reasonable density estimates. This may also be inferred from the fact that the distance between two H-bridged tetracarboxylic-acid molecules amounts to 10.0 Å, almost identical to the preferred contact distance between two C_{60} molecules. However, complex formation is *not* observed in this case, which might be attributed to the obvious lack of CT possibilities. Evidently, the nature of the face-to-face (FTF) HQ/C_{60} interactions in $(HQ)_3C_{60}$ is important in regard of the conductivity properties of the complex, and sufficient charge transfer could be expected to raise the conductivity. Results of preliminary conductivity measurements on $(HQ)_3C_{60}$ are briefly reported in the following section.

The separation between the C_{60} centers and the encapsulating equatorial ETF-oriented HQ molecular centers is $a/2 = 8.108$ Å (*Fig. 1*) leading to a distance of 4.6 Å between the center of the orthogonal HQ molecules and the C-surface of C_{60}. This ETF approach of HQ and C_{60} is quite narrow as evidenced by a comparison with pairwise ETF aggregates of benzene/benzene, benzene/naphthalene, and benzene/anthracene, for which corresponding distances between 4.8 and 5.0 Å have been estimated [11]. In summary, it appears qualitatively very plausible that the twelve close HQ/C_{60} contacts in $(HQ)_3C_{60}$ more than make up for the loss of six C_{60}/C_{60} contacts and the weakening of the remaining six C_{60}/C_{60} contacts, such that complex formation becomes favorable. The short host-guest contacts in $(HQ)_3C_{60}$ explain the remarkably high density, which was also rationalized above by comparison of the 'strained' (expanded) HQ host architecture of the present complex with the normal 'unstrained' one of the β-form of HQ itself. Thus, the tight packing of $(HQ)_3C_{60}$ becomes evident once again. However, as we have seen, the fact that the C_{60} molecules are so firmly locked up in the super-cube cavities of the HQ host network cannot prevent orientational disorder of the spherical guest. One would naturally conclude that this disorder is of static nature. Should this indeed be the case, temperature variation would not much affect the disorder, and *e.g.* low-temperature X-ray studies could probably provide little as regards the measurement of detailed structural data (individual bond lengths) of C_{60} in the present complex $(HQ)_3C_{60}$.

We have seen that the C_{60} molecules in $(HQ)_3C_{60}$ are surrounded by six molecules of HQ in FTF manner and another six in ETF fashion, such that these 12 HQ molecules run along the edges of the super-cube enclathrating the C_{60} molecule. These edges extend from an H-bonded $(OH)_6$ ring to a neighboring, HQ-bridged one and are equal to the rhombohedral cell edge a' (10.438 Å, *Figs. 3* and *4*). The twelve HQ molecules encapsulating a C_{60} sphere may be grouped into six centrosymmetric 'sandwiches', three of FTF and three of ETF type, between which the C_{60} molecule is interposed. On the other hand, every HQ molecule is sandwiched by two C_{60} molecules in FTF fashion, and by another two in ETF manner. Obviously, this is in keeping with the 3:1 HQ/C_{60} stoichiometry of the complex. The sandwiching of the HQ molecules by C_{60} is reflected in the shape and orientation of the C vibrational ellipsoids of HQ (*Fig. 2*) inasmuch molecular and atomic motion appears to be small perpendicular to the long O–O axis of HQ. It is this axis around which the four sandwiching C_{60} molecules are grouped in a belt-like fashion. Finally, it is noted that every C_{60} molecule may of course also be viewed to be sandwiched by two polar $(OH)_6$ rings (*Figs. 1*, *3*, and *4*), and the respective contacts are improved by the marked chair-like puckering of these large rings (see above, *Fig. 3a, b*). The six closer polar O/C_{60} approaches within a super-cube measure 3.6 Å.

We conclude the discussion of the supramolecular crystal architecture of $(HQ)_3C_{60}$ with a closer look at the self-coordination of the C_{60} molecules. It has been pointed out above that the C_{60} spheres set up a trigonally compressed super-polonium framework with the same dimensions as that of the H-bonded HQ host network. The distance between C_{60} contact neighbors in the HQ complex (10.483 Å) is *ca.* 0.3–0.4 Å longer than in C_{60} itself leading to a separation of the C_{60} C-surfaces of *ca.* 3.4 Å, which is similar to the π-stacking distance of graphite (3.35 Å). The building blocks of the C_{60} super-polonium framework in $(HQ)_3C_{60}$ are trigonally compressed super-cubes with the C_{60} globes occupying the corners. Every C_{60} molecule is, therefore, (self-) coordinated to six translationally equivalent (along the rhombohedral cell edge a') C_{60} contact neighbors in trigonally compressed octahedral fashion. This coordination is illustrated by the space-filling stereoview of *Fig. 5*. The octahedral sixfold self-coordination of C_{60} in $(HQ)_3C_{60}$ may be referred to as a 'thin' sphere packing [12] in contrast to a 'dense' closest packing with twelvefold coordination. This thin C_{60} selfpacking in $(HQ)_3C_{60}$ leaves open enough room for allowing the geometrically equivalent, H-bonded HQ super-polonium network to interpenetrate symmetrically, such that on the whole a tightly packed 'mixed' double super-polonium host-guest architecture emerges for the complex. All C_{60} molecules of $(HQ)_3C_{60}$ are, therefore, in three-dimensional π-contact throughout the crystal, which is relevant as regards interesting electrical and magnetic properties, *i.e.* conductivity and ESR behavior. It has been speculated further above that slight outward bulges of the C_{60} spheres could possibly improve (shorten) their π-contacts with neighboring spheres, yet no support for this idea may be derived from our crystal-structural measurements due to the C_{60} orientational disorder.

Conductivity, ESR[2]). First preliminary conductivity measurements on powdered samples of $(HQ)_3C_{60}$ did not yield σ values above 10^{-6} Scm^{-1}. This might perhaps have in part to do with the lengthened contact distances of the C_{60} molecules in the complex (10.4 Å, see structural discussion above). In the highly conductive salt K_3C_{60}, the separation of contacting C_{60} spheres is only 10.1 Å [13], almost as short as in C_{60} itself. The lack of significant conductivity is in accordance with the low spin concentration of less than 10^{-4} spins/molecular unit, as extracted from ESR spectra of single crystals of $(HQ)_3C_{60}$. It is well worth mentioning, however, that the ESR signals are as narrow as 5 mT, usually the case for extremely averaged fine or hyperfine interactions known from one-dimensional organic conductors. Taking into account the observation that g-factor anisotropy is almost missing, it may be concluded that these spins are preferentially localized on the C_{60} spheres. It is finally noted that the detection of ESR signals in crystalline $(HQ)_3C_{60}$ might provide further support for the CT-type interactions between the HQ (π-donor) host and C_{60} (π-acceptor) guest molecules, as inferred above from structural and other data; the deep black color of the complex may result from a CT in the excited singlet state $^1(d^+a^-)$. Temperature-dependent conductivity and ESR experiments will turn these preliminary views into a clearer picture.

Conclusions. – The successful preparation of the complex $(HQ)_3C_{60}$ clearly opens up possibilities for a whole range of other donor-acceptor complexes of C_{60} (and other fullerenes) with potentially interesting properties. Calixarenes or tetrathiafulvalenes would be attractive donors, for example. It is noted that simple solution experiments with π-donating solvents produce interesting color effects. Whereas C_{60} gives magenta-colored solutions in π-accepting nitrobenzene and benzonitrile, as well as in benzene and toluene, the following deviating colors are observed with stronger π-donating solvents: bluish violet (anisole, phenol, thiophenol); brownish, slightly greenish yellow (*o*-dimethoxyben-

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[2]) I am indebted to *J. U. von Schütz*, Stuttgart, for undertaking these investigations.

zene); deep brownish orange (molten *p*-dimethoxybenzene). It would be interesting to record the UV/VIS spectra of these solutions and to analyze them in regard of charge-transfer effects. We are currently attempting to grow (complex?) crystals from the dimethoxybenzene solutions. In addition to hydroquinone, we have attempted to crystallize molecular complexes of C_{60} with *p*-phenylenediamine and *p*-aminophenol. There are indications that complex crystals may have formed, yet they were of low grade.

We are tempted to close this report by referring to the fascinating complex $(HQ)_3C_{60}$ as the apotheosis of the classical inclusion chemistry of hydroquinone, fully 142 years after *Wöhler*'s first report [14] of guest accomodation by this simple phenol.

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