Host–Guest Compounds

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A Spherical Molecule with a Carbon-Free I_h-C_{80} Topological Framework[**]

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Dedicated to Professor Helmut Werner on the occasion of his 75th birthday

The discovery of novel fullerene carbon allotropes and the exploration of their reactivity and chemical properties is a success story of the last two decades.[1] Within the rapidly growing class of fullerenes, the most stable and therefore accessible molecules are those that fulfill both the isolated pentagon rule (IPR), which describes the stability of the σ core, and the criterion of spherical aromaticity of the π system of these molecules. In contrast, those fullerenes that only follow the IPR are less stable and, therefore, less accessible. The non-aromatic C_{80} molecule is one of the derivatives which has long been of interest in this chemistry. Of the seven structural isomers (D_{5d}, C_{2v}(I), D_2, C_{2v}(II), D_{5h}, D_3, and I_h) satisfying the IPR, the D_2 isomer was isolated in small quantities in 1996 by Kappes and co-workers.[2] In 2000, Shinohara and co-workers[3] reported on the synthesis of the D_{5d} isomer, in which they also obtained the D_2 isomer. According to quantum chemical calculations[4] the first six isomers are all stable within an energy range of $30\,\text{kJ}\,\text{mol}^{-1}$. The icosahedral isomer, however, is calculated to be $72\,\text{kJ}\,\text{mol}^{-1}$ less stable than the energetically most favored D_{5d} isomer and has never been reported. Lately, endohedral C_{80}[5] has been synthesized using a four-atom trimetallic nitride cluster as a guest inside the fullerene cage.[6] In this case the I_h-symmetric isomer was also found in low yields; however, no crystallographic confirmation has been obtained for these spherical systems. Only by the functionalization of the endofullerenes $La_2@C_{80}$[7] and $Sc_4O@C_{80}$[8] was it possible to receive structural information about such derivatives by X-ray crystallography in order to confirm the original icosahedral symmetry.

Some time ago we were able to show the synthesis of the soluble, spherical molecules of the formula $[\{Cp^RFe(\eta^5:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1\text{-}P_5)\}_{12}(CuX)_{10}(Cu_2X_3)_5\{Cu(CH_3CN)_2\}_5]$ (**1**: $Cp^R = Cp^* = \eta^5\text{-}C_5Me_5$, X = Cl (**a**),[9a] $Cp^R = \eta^5\text{-}C_5Me_4Et$, X = Br (**b**)[9b]), which consist of 90 non-carbon core atoms and feature two half shells of fullerene-like topology. These spherical molecules are only formed by applying the proper stoichiometry and dilution conditions of the starting materials (pentaphosphaferrocene and the Cu^I halide); otherwise coordination polymers are obtained.[10] When a *cyclo*-P_4 ligand complex is used as starting material, a carbon-free C_{32} analogue can be isolated.[11] A larger but incomplete spherical molecule $C_{60}@[Cu_{26}Cl_{26}L_2\{Cp^*Fe(\eta^5\text{-}P_5)\}_{13}(CH_3CN)_9]$ (**2**, $L = H_2O$) was formed using C_{60} as a nucleus for the aggregation of pentaphosphaferrocene and copper(I) chloride building blocks.[12] Thus, it becomes evident that larger spherical molecules that have fullerene topology and consist of non-carbon atoms are only accessible using larger guest molecules in a template-controlled aggregation reaction.[13] Since the *ortho*-carborane *o*-$C_2B_{10}H_{12}$ has the proper size (ca. 0.8 nm)[14] as well as the required pseudo-fivefold symmetry to be encapsulated into a spherical supermolecule, the reaction of $[Cp^*Fe(\eta^5\text{-}P_5)]$ with CuCl was carried out in the presence of *o*-$C_2B_{10}H_{12}$. In this way, the formation of dark brown, cubic crystals of the composition $C_2B_{10}H_{12}@[\{Cp^*Fe(\eta^5:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1\text{-}P_5)\}_{12}(CuCl)_{20}]$ (**3**) are found. As a side product, very thin needles of a compound similar in composition to **1a** (referred to as **1a′**) are obtained. Compound **1a′** is identified by its solution and solid-state NMR spectra,[15] which agree well with the published data.[9a] Moreover, X-ray structural data gives evidence for its identity.[15] The two compounds were separated by dissolving **1a′**, whereas **3** is insoluble in common solvents.

Compound **3** crystallizes in the cubic space group $Fm\bar{3}c$.[16] Surprisingly, the spherical supermolecules of **3** form a primitive cubic packing motif in the crystal lattice. The large cavities between the molecules are filled by solvent molecules. Figure 1a displays the molecular structure of **3**. The *ortho*-carborane is located in the middle of the inorganic host molecule $[\{Cp^*Fe(\eta^5\text{-}P_5)\}_{12}\{CuCl\}_{20}]$, which shows icosahedral-like symmetry.[17] This host molecule of **3** consists of 12 pentaphosphaferrocene units and 20 CuCl units and the framework is an entirely carbon-free analogue of the icosahedral C_{80} molecule. In **3**, each phosphorous atom of the planar *cyclo*-P_5 ligand of the pentaphosphaferrocene molecule is coordinated to the metal centers of CuCl. By further coordination of phosphorous atoms of other *cyclo*-P_5 rings, six-membered Cu_2P_4 rings are formed. Owing to the distorted tetrahedral coordination geometry around the Cu atoms, these six-membered rings are folded along the Cu⋯Cu axis by about 137°. The core of the host molecule consists of

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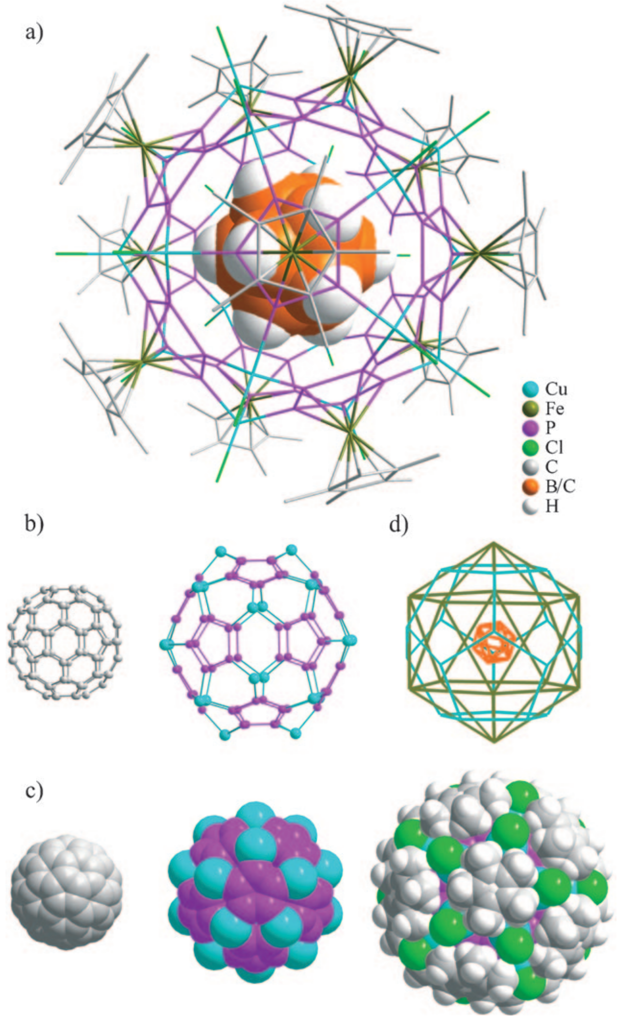

Figure 1. a) Molecular structure of $C_2B_{10}H_{12}$@$[\{Cp^*Fe(\eta^5:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1\text{-}P_5)\}_{12}(CuCl)_{20}]$ (**3**; space-filling model for the encapsulated *o*-carborane, wire/stick model for the inorganic supermolecule); H atoms of the host molecule are omitted for clarity. b) Comparison of the icosahedral symmetric structures of I_h-C_{80} (left) and the inorganic core $Cu_{20}P_{60}$ of **3** (right); $C_2B_{10}H_{12}$ and Cl atoms as well as the Cp*Fe fragments are omitted for clarity. c) Comparison of the sizes (outer diameter, space-filling-model) of the spherical molecules of C_{80} (left; 1.1 nm), the $Cu_{20}P_{60}$ core of **3** (middle; 1.62 nm) and the complete molecule of **3** (right; 2.3 nm).[19] d) View of the interpenetrated dodecahedron of 20 Cu atoms in the icosahedron of 12 Fe atoms, which encapsulate the pseudo-icosahedron the of *o*-carborane.

12 five-membered rings (*cyclo*-P_5 rings as building blocks) and 30 six-membered rings (Cu_2P_4 units), exactly like in the icosahedral C_{80} isomer. Figure 1b displays the similarities between the icosahedral C_{80} molecule and the inorganic host molecule of **3**. The P–P bonds in **3** are between 2.086(5) and 2.103(4) Å. They are, therefore, slightly shorter than those in the uncoordinated *cyclo*-P_5 ligand complex $[Cp^*Fe(\eta^5\text{-}P_5)]$ (2.117(4) Å),[18] as are the observed P–P bonds in the inorganic supermolecule with encapsulated C_{60} (**2**; 2.105(9)–2.126(8) Å).[12] They are, however, in the same range as the P–P bonds in the spherical molecule **1a** (2.072(6)–2.122(6) Å).[9a] The Cu–P bond lengths of **3** range from 2.282(3) to 2.307(4) Å, which are comparable to those in **2** (2.201(7)–2.389(9) Å)[12] and **1a** (2.264(5)–2.319(5) Å).[9a] The Cu–Cl bonds in **3** (2.195(4) and 2.195(6) Å) are slightly shorter than those in **2** (2.199(4)–2.359(5) Å)[12] and in **1a** (2.189(5)–2.255(5) Å (terminal CuCl moieties), 2.294(6)–2.353(6) Å (bridging Cu_2Cl units)).[9a]

Figure 1c depicts a size comparison between I_h-C_{80} (left), the $Cu_{20}P_{60}$ core of the carbon-free C_{80} analogue **3** (middle), and the complete spherical molecule of **3** (right). The outside diameter of **3** (2.3 nm) is about two times larger than that of C_{80} (1.1 nm), whereas the core is still 1.6 nm in size.[19] The size of **3** corresponds well with that of **2** (2.3 nm) and is larger than **1a** (2.14 nm). The inner cavity of **3** appears to be almost spherical with a diameter of about 0.82 nm, which is much smaller than the inner diameter of **2** (1.35 nm). The inner cavity of **3** is just big enough for the *ortho*-carborane molecule (0.795 nm) to be completely encapsulated. The formation of the icosahedral shell molecule can be visualized by joining two half shells of molecule **1** together while rotating one shell by 36°. The same shells are joined by five $Cu(CH_3CN)_2$ and five Cl entities to yield molecule **1a**. The constitution of supermolecule **3** is similar to the family of keplerates.[20,21] It is formed by an icosahedron of 12 Fe atoms (the edges are centered over pentagons of the *cyclo*-P_5 rings) and an interpenetrated dodecahedron of 20 Cu atoms in which the pseudo-icosahedron of the *o*-carborane is encapsulated (Figure 1d).

Compound **3** is surprisingly insoluble in all common solvents. Besides its X-ray structure analysis, the compound was characterized by solid-state NMR spectroscopy. In the $^{11}B\{^1H\}$ MAS NMR spectrum of **3**, weak and broad signals for encapsulated *o*-$C_2B_{10}H_{12}$ are observed at $\delta = -7.4$, -14.3, -18.8, and -19.7 ppm (for assignment see reference [15]). In contrast, the signals of free *o*-$C_2B_{10}H_{12}$ are found at $\delta = -2.5$, -9.2, -13.5, and -14.5 ppm, in good agreement with literature data.[22,23] The upfield shift of about 5 ppm of the four signals indicates a diamagnetic shielding of the boron nuclei of *o*-$C_2B_{10}H_{12}$ arising from interaction with the inorganic host molecule. Apparently, a partial charge transfer from the inorganic shell molecule to the encapsulated guest takes place, which resembles the behavior of the C_{60} guest in **2**.[12] In light of literature reports on the chemical reduction of *o*-$C_2B_{10}H_{12}$ by sodium in THF to form the anion $[C_2B_{10}H_{12}]^{2-}$,[24] this charge transfer is feasible. A comparison of the chemical shifts of the encapsulated carborane in **3** with those of the carborane anions is not possible owing to the ongoing rearrangement of the atoms in the anion, which leads to a mixture of isomers after oxidative workup. In the ^{31}P MAS NMR spectrum of **3**, a broad signal is observed at $\delta = 113$ ppm that is different from the signal of the side product **1a′** (68 ppm).[9a] The $^{13}C\{^1H\}$ MAS NMR spectrum of **3** displays two broad signals at 93 and 13 ppm, which can be assigned to the Cp* ligands. Unfortunately, the signals for the carbon atoms of the *o*-carborane are not observed owing to the low natural abundance of the ^{13}C nucleus and the low ratio of the only two carbon atoms in the carborane to the 120 carbon atoms in the inorganic host molecule of **3**. The ^1H MAS NMR spectrum of **3** shows two very broad and unstructured signals at $\delta = 7$ and 1.5 ppm which overlay the signals of the carborane (cf. free $C_2B_{10}H_{12}$: 1.4–3.6 ppm). The

IR spectrum of **3** reveals the ν(B–H) (2592 cm^{-1}) and ν(C–H) (3042 cm^{-1}) stretching modes. In comparison to the free *o*-carborane (2600 cm^{-1} (ν(B–H)), 3070 cm^{-1} (ν(C–H))), a shift to lower wavenumbers is observed. This finding also indicates an electronic interaction between the inorganic host molecule and the encapsulated carborane.

In summary, the concept of template-controlled aggregation[13] has been shown to be an efficient route to unprecedented large and entirely spherical molecules of fullerene-type topology. The inorganic shell of 80 non-carbon core atoms of **3** consists of 12 five-membered *cyclo*-P_5 rings and 30 six-membered Cu_2P_4 rings and has a size of 2.3 nm with an inner cavity of 0.82 nm. This void accommodates the *ortho*-carborane template (ca. 0.8 nm). Electronic interaction between the inorganic shell and the encapsulated guest molecule in **3** is determined by MAS NMR and IR spectroscopy. The composition and size of the fullerene-type product is controlled by the size of the guest molecule, which will be important for future investigations.

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[14] The outer diameter of *o*-$C_2B_{10}H_{12}$ was calculated as the longest H···H distance (0.555 nm) plus twice the van der Waals radius of H (0.12 nm).

[15] See the Supporting Information.

[16] Crystal structure analysis of a single crystal (0.12 × 0.10 × 0.03 mm) of **3** was performed on an Oxford Gemini R Ultra CCD diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). The structure was solved by direct methods with the program SHELXS-97,[25a] and full-matrix least-squares refinement on F^2 in SHELXL-97[25b] was performed with anisotropic displacements for non-H atoms. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model. Unit cell dimensions: cubic, space group $Fm\bar{3}c$ (No. 226); $a = b = c = 41.4625(9)$ Å, $\alpha = \beta = \gamma = 90°$, $T = 103(1)$ K, $Z = 8$, $V = 71\,280(3)$ Å^3, $\rho_{calcd} = 1.156$ Mg m^{-3}, $\mu(Cu_{K\alpha}) = 9.138$ mm^{-1}, 17105 independent reflections ($R_{int} = 0.1522$, $2\theta_{max} = 103.3°$), 1728 observed with $F_o = 4\sigma(F_o)$; 103 parameters, $R_1 = 0.0740$, $wR_2(F > 4\sigma(F_o)) = 0.2138$. CCDC 716718 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[19] The outer diameter of the **3** was calculated as the distance between two opposing methyl hydrogen atoms (2.06 nm) plus twice the van der Waals radius for H (2 × 0.12 nm). The inner diameter of the inorganic shell molecule of **3** was determined as twice the shortest distance between the theoretical center of the molecule and the phosphorus atoms minus twice the van der Waals radius for P (2 × 0.18 nm). The outer diameter of C_{80} in I_h symmetry was determined as the largest C···C separation in C_{80} (0.79 nm) plus twice the van der Waals radius of C (2 × 0.17 nm).

[20] Keplerates are double-spherical polyhedra containing platonic and archimedean solids such as an icosahedron and an icosidodecahedron, or in the present case, an icosahedron and a dodecahedron.

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