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Communication

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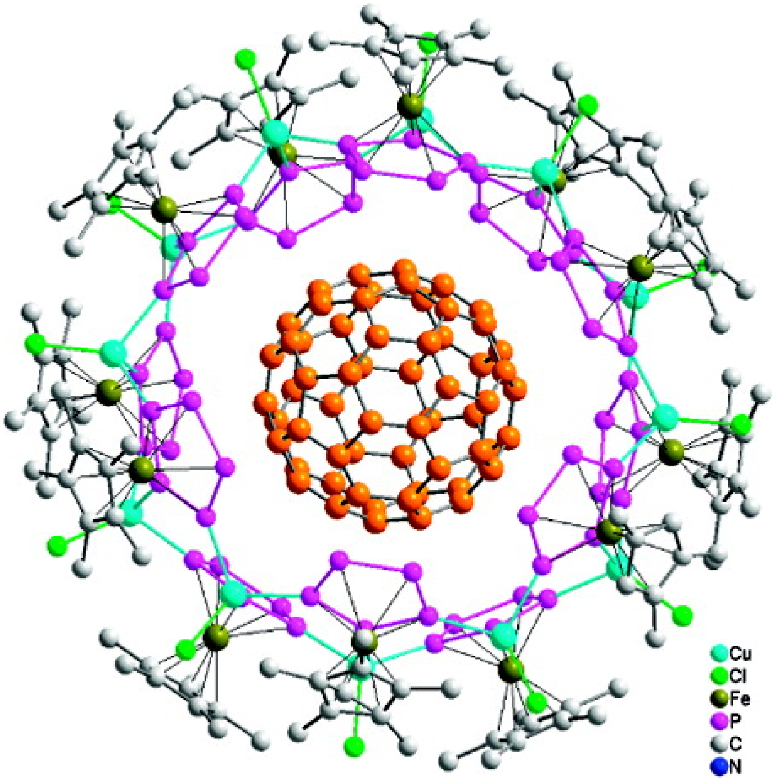

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COMMUNICATIONS

Fullerene C_{60} as an Endohedral Molecule within an Inorganic Supramolecule

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The synthesis and properties of large spherical molecules and giant clusters is a fascinating field in contemporary chemistry, unifying all areas of organic/supramolecular, inorganic, and coordination chemistry as well as organometallic chemistry. Recent developments of low-valent group 13 metalloid clusters,[1] chalcogeno-bridged copper, and silver clusters[2] as well as giant polyoxomolybdates[3] represent the largest structurally characterized clusters reported so far. Owing to its unique chemical and physical properties, buckminsterfullerene C_{60} has found wide applications ranging from superconductivity to medicine and biology.[4] Three types of organometallic fullerenes are presently known: (i) fullerides,[5] (ii) endohedral metal−fullerene complexes in which metal atoms or metal-containing clusters are encapsulated inside the fullerene,[6] and (iii) exohedral metallofullerenes,[7] in which metal moieties are attached to the fullerene exterior. Furthermore, fullerenes have had a significant impact in supramolecular chemistry,[8] in that weak donor−acceptor associates have been formed with receptors such as calixarenes, porphyrins, crown ethers, and other electron-donating π-systems.[9] We report herein the first example of a complete encapsulation of C_{60} itself by an inorganic fullerene-like system via molecular recognition of the five- and sixfold-symmetric structural motif of C_{60}. The product $C_{60}\subset[Cu_{26}Cl_{26}L_2\{Cp^*Fe(\eta^5\text{-}P_5)\}_{13}(CH_3CN)_9]$ ($L = H_2O$) exhibits an inorganic cover consisting of 99 inorganic core atoms from pentaphosphaferrocene and Cu(I) chloride building blocks. The overall spherical molecule possesses an outer diameter of 2.3 nm and shows a remarkable electronic interaction between C_{60} and the encapsulating giant molecule.

We recently reported the use of $[Cp^xFe(\eta^5\text{-}P_5)]$ in the formation of the soluble, fullerene-like cage compounds $[\{Cp^xFe(\eta^5{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}P_5)\}_{12}\{CuX\}_{10}\{Cu_2X_3\}_5\{Cu(CH_3CN)_2\}_5]$ (**1**: $Cp^x = Cp^*$, $X = Cl$ (**a**),[10] $Cp^x = \eta^5\text{-}C_5Me_4Et$, $X = Br$ (**b**),[11] which possess a 90-atom core consisting entirely of non-carbon atoms. The outer diameter of **1a** of about 2.14 nm is three times larger than that of C_{60} (0.7 nm), while the inner cavity has a diameter of 1.25 nm. Each of these spherical moieties encapsulates a molecule of $[Cp^xFe(\eta^5\text{-}P_5)]$, but no solvent molecules, although numerous were found in the crystal lattice of the compounds. The long reaction times in the formation of **1a**,**b** (2 weeks by diffusion techniques) raise the question of whether the pentaphosphaferrocene molecules are incidentally incorporated in the spherical molecule or whether a molecule of fivefold symmetry is required in order to form a spherical cluster via molecular recognition. Short reaction times and concentrated solutions lead to the formation of polymeric compounds in which not all of the P atoms of the *cyclo*-P_5 rings are coordinated to Cu centers.[12]

Since C_{60} has the proper size and symmetry to be incorporated into a spherical molecule such as **1**, we sought to verify the abovementioned hypothesis by carrying out the reaction of $[Cp^*Fe(\eta^5\text{-}P_5)]$ with CuCl under dilute conditions in the presence of C_{60}. In this way, the exclusive formation of black crystals of a soluble, supramolecular assembly of the composition $C_{60}\subset[Cu_{26}Cl_{26}(H_2O)_2\{Cp^*Fe(\eta^5\text{-}P_5)\}_{13}(CH_3CN)_9]$ (**2**) was found in about 45% isolated yield, with no evidence of **1a** as a byproduct.[13]

Compound **2** crystallizes in the orthorhombic space group *Pnma* with 24 *o*-dichlorobenzene and four acetonitrile solvent molecules in the unit cell. The pseudo-spherical molecules of **2** form a distorted body-centered cubic packing motif in the crystal lattice.

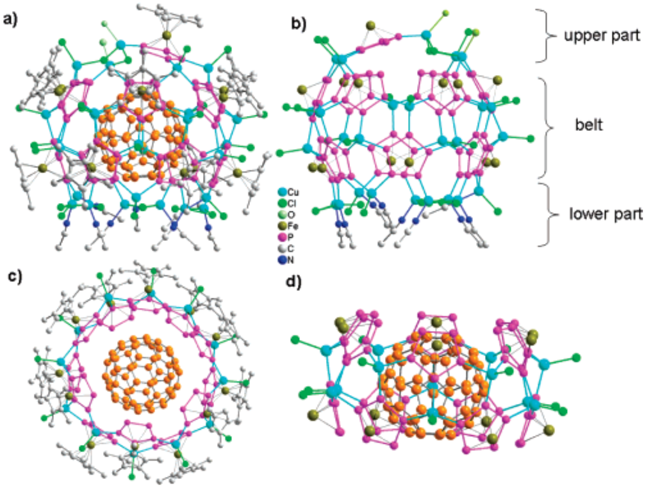

Figure 1. (a) Molecular structure of **2** (ball-and-stick); H atoms have been omitted for clarity. (b) Simplified view of the cover molecule of **2** (ball-and-stick); Cp* fragments have been omitted for clarity. (c) View of the belt-like core of **2** surrounding the C_{60} molecule; the upper and lower part have been omitted, and the C atoms of C_{60} are highlighted in orange. (d) Orthogonal view of the structure shown in (c); the Cp* ligands are additionally omitted.

Figure 1a displays the molecular structure of $C_{60}\subset[Cu_{26}Cl_{26}(H_2O)_2\{Cp^*Fe(\eta^5\text{-}P_5)\}_{13}(CH_3CN)_9]$ (**2**). The entire molecule is located on a mirror plane. The host molecule of **2** can be formally divided into three parts (Figure 1b). The upper part consists of a $\{Cp^*Fe(\eta^5\text{-}P_5)\}$ fragment coordinated via three phosphorus atoms to two {CuCl} units and one $\{Cu_3(\mu\text{-}Cl)_2(H_2O)_2Cl\}$ unit.[13] One coordinated water molecule is symmetrically disordered over two positions together with terminal Cl. The middle portion resembles a belt and consists of 12 $\{Cp^*Fe(\eta^5\text{-}P_5)\}$ and 12 {CuCl} units with idealized D_{6d} point symmetry of a hexagonal antiprism (Figure 1c,d). The lower part contains three $\{Cu(CH_3CN)Cl\}$ and three $\{Cu_2(\mu\text{-}Cl)_2(CH_3CN)_2\}$ units with an almost ideal C_{3v} point symmetry. It is only the low symmetry of the upper part that reduces

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the symmetry of the whole molecule to C_s. All parts are joined together by Cu−P bonds. The P−P bond lengths of the *cyclo*-P_5 rings in **2** are between 2.105(9) and 2.126(8) Å and are therefore comparable to those of the similarly substituted complex [(η^5-C_5Me_4Et)Fe(η^5-P_5)] (2.088(3)−2.108(3) Å)[14] as well to those found in the spherical molecule **1a** (2.072(6)−2.122(6) Å).[10] The Cu−P bond lengths of **2** are within 2.201(7)−2.389(9) Å, which compares well to those in **1a** (2.264(5)−2.319(5) Å). The disordering of the encapsulated C_{60} molecule of **2**, which could be refined in two positions, indicates its rotational mobility.

The main difference between **2** and **1a,b** is the larger size of the entire molecule and the inner cavity. Thus, the outside diameter of **2** (2.3 nm) is somewhat larger than that of the comparable compound **1a** (2.14 nm) and similar to the bromine derivative **1b** (2.37 nm).[15] The inner cavity of **2** appears to be almost spherical (Figure 1c) with a diameter of about 1.35 nm. The gap between C_{60} and the internal surface of **2** is between 5.06 (to μ-Cl) and 5.25 Å (to P). Regarding the sum of van der Waals radii of Cl/P and C, the fullerene molecule inside **2** is allowed to rotate freely. Subsequently, the observed crystallographic disordering of C_{60} is a result of its free rotation.

Compound **2** is soluble in mixtures of acetonitrile and CH_2Cl_2. In the ^{31}P NMR spectrum of **2**, a broad signal at 83 ppm was observed which resembles that of **1a** (68 ppm).[10] In the ^{13}C NMR spectrum of **2**, a signal at 140.6 ppm for the C_{60} moiety was recorded. When free C_{60} was added to the NMR sample of **2**, an additional signal at 143.3 ppm was observed, which indicates that no exchange of C_{60} occurs and a remarkable upfield shift by about 2.7 ppm in comparison to free C_{60} in the same solvent mixture. A similar distinction was found in the solid state. In the ^{13}C MAS NMR spectrum of **2**, the chemical shift of the encapsulated C_{60} was observed at 141.1 ppm, which is shifted in comparison with that of pure C_{60} (144.1 ppm[16]). Furthermore, the Raman spectrum of **2** displays a shift of the characteristic $A_g(2)$ mode of C_{60} in **2** (1460 cm^{-1}) by 8 wave numbers to lower energy when compared to free C_{60} (1468 cm^{-1}).[17] Both results reflect the significant interaction between C_{60} and the cover of the inorganic supramolecule by charge transfer to C_{60}.[18] The change in the properties of the guest molecule was further supported by voltammetric measurements. Compound **2** undergoes a chemically reversible, but electrochemically irreversible ($\Delta E_p \geq 320$ mV) reduction at a peak potential $E_{p,c}$ of −0.91 V. With reference to cluster **1a**, which is reduced by 12 electrons in its first cathodic wave, this process in **2** is assigned as a multielectron process involving the inorganic $[Cu_{26}Cl_{26}(H_2O)_2\{Cp^*Fe(\eta^5\text{-}P_5)\}_{13}(CH_3CN)_9]$ cover. UV/vis/NIR spectroelectrochemistry indicated some intensity loss of the electronic bands of **2** at 284, 322, and 383 nm without any apparent shift of the peak maxima. When, following the first reduction, the potential was increased to about −1.3 V, a new absorption band at 1080 nm grew, which is characteristic of the $C_{60}^{\bullet-}$ radical anion.[19] The onset potential matches that of a reversible wave at $E_{1/2} = -1.25$ V observed in voltammetry that is associated with considerably lower peak currents compared to the first reduction. This feature is thus assigned as the reduction of the encapsulated C_{60} molecule. We note a large cathodic shift of the $C_{60}/C_{60}^{\bullet-}$ couple with respect to C_{60} itself, which in the same CH_3CN/1,2-$C_6H_4Cl_2$ (3:1)/NBu_4PF_6 electrolyte undergoes four reversible reductions at −0.99, −1.395, −1.86, and −2.32 V.[15] This shift probably arises from electrostatic repulsion caused by C_{60} encapsulation inside a negatively charged cluster sheet and a slowing of the electron transfer rate, though charge transfer may also contribute.

The results have shown that [Cp*Fe(η^5-P_5)] can be employed in the coordination chemistry with copper(I) halides for the assembly of supramolecular host molecules to cover molecules such as C_{60} that bear a similar symmetry. Since the reaction of [Cp*Fe(η^5-P_5)] with CuCl in the presence of C_{60} leads exclusively to the C_{60}-encapsulating supramolecule **2** with no evidence of the spherical fullerene-like molecule **1a**, which is formed in the absence of C_{60}, one can conclude that a template-supported synthesis has occurred via molecular recognition of a five- and sixfold-symmetric template. The thus formed supramolecule **2** contains completely encapsulated C_{60}, which is, on the one hand, a unique endohedral molecule and, on the other hand, an acceptor of electron density from an inorganic cover in a remarkable manner for C_{60} host−guest systems.

Acknowledgment. This work was comprehensively supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We are grateful to Dr. R. Köppe (University of Karlsruhe) for measurement of the Raman spectra, and to Prof. E. Brunner and C. Gröger (University of Regensburg) for the MAS NMR measurements.

Supporting Information Available: Crystallographic details, experimental details, and voltammetric measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) We found in several independent reactions single crystals of **2** in the same crystallographic space group carrying the identical disordering between Cl and H_2O. The assignment of H_2O is based on the finding of no further atoms close to it, as required in, e.g., CH_3CN. The appearance of H_2O is probably connected with the employed purification procedure of commercial Cu(I)Cl: washing with aqueous HCl (half-concentrated), followed by washings with H_2O, EtOH, and Et_2O. The exclusive formation of **2** was proven by X-ray crystallography and ^{31}P MAS NMR spectroscopy.
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(18) For example, the adduct $[(Cp_2Fe)_2C_{60}]$ shows almost no difference in the ^{13}C MAS chemical shift for C_{60} and a shift to lower energy of 4 cm^{-1} for the $A_g(2)$ mode.[9e] For C_{60}•TDAE, where one electron is transferred to C_{60}, the low-energy shift of the $A_g(2)$ mode is about 14 cm^{-1}.[9e,17b] Examples for reported upfield shift differences in the ^{13}C NMR for free C_{60} and C_{60} host molecules are 1.4[9f] and 0.53 ppm.[9d]
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