Although C₆₀ is readily available from the vaporization of graphite and the combustion of hydrocarbons in fuel-rich flames, these methods are unselective and relatively uncontrollable. Considerable progress has been made over the last few years towards the total synthesis of C₆₀ in isolable quantities,[1] however, chemical synthesis in bulk amounts remains elusive and challenging even today. One rational approach is the synthesis of two identical C₃₀H₁₂ units, which could then be fused together to form the fullerene.[2–4] Thus, the study and synthesis of buckybowls, potential precursors of fullerenes and larger π systems, is essential, and many of them have attained key positions in the literature.[5–7]

The C₃₀H₁₂ geodesic polyarene 1 is one of several possible hemifullerene isomers.[6a,d] Considerable effort has been directed toward studies on the ligating properties and reactivity of the smaller fullerene fragment corannulene, C₂₀H₁₀,[8] but hardly any transition-metal complexes of C₃₀H₁₂ isomers have been prepared. Only recently was the first π complex of 1 with rhodium[9] isolated, and charging of 1 with alkali metals has never been examined.

Self-aggregation into supramolecular structures has also recently found large interest. Supramolecular chemistry plays roles in molecular and chiral recognition,[10] bioorganics and biomimetics,[10i,11] reactivity and catalysis,[10i–k,11c,d,12] and transport.[10j,k,11b,13] A particularly intriguing facet of this field is the ability of alkali metal ions to act as “electrostatic paste” to hold together two or more organic anions.[14,15] Polycyclic aromatic hydrocarbons (PAHs) constructed in a stack are held together by countercharged metal ions that stabilize high negative charges on the anions. As the total electrostatic interaction between PAH anions and alkali metal cations depends on the square of the degree of reduction, it is clear why some PAHs show an inclination to aggregate only at high charges.[16] The PAH anions that do aggregate are typically unstable in solution and tend to precipitate.[14] so higher order stable aggregates with Li⁺ ions, even more so with K⁺ ions, are scarce.[17] Herein we describe the self-assembly and structure of a unique tetrameric aggregate of hemifullerene hexaanions with potassium cations that has high charge density, pyramidalization, and surprising stability in solution.

Hemifullerene 1 (C₃₀H₁₂, Figure 1a) undergoes an extremely slow charging process with potassium metal to give a hexaanion.[18] Quenching of the hexaanion with water[19] cleanly yields a hexahydro derivative (C₃₀H₁₈) that is isomeric with 2,[20] as verified by desorption chemical ionization high resolution mass spectrometry (DCI-HRMS calculated: 379.1487, found: 379.1519). The absence of any other signal in the m/z 372–389 region indicates that none of the C₃₀H₁₂ was quenched back to 1 and confirms that the degree of charge was indeed hexaanionic. The exact structure of the...
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C_{60}H_{18} product obtained is uncertain; however, it is clear from the $^1$H NMR spectrum that this new species is neither 1 nor 2.

Reduction of 1 with lithium gives no new diamagnetic species, even after months of contact with the alkali metal, heating, sonication, and/or the aid of corannulene. Charging with potassium, on the other hand, gives rise to the stable hexaanion, albeit only after a long period of charging and heating to room temperature (Figure 1b). No other diamagnetic species is observed before the hexaanion is reached.

From molecular orbital calculations on 1, the LUMO, LUMO+1, and LUMO+2 were found to be effectively degenerate for the neutral hydrocarbon as the degenerate LUMO+1 and LUMO+2 lie only 2.7 kcal mol$^{-1}$ (0.116 eV) above the LUMO. This suggests that every anion from $\text{K}^+$ to $\text{K}^{6-}$ could have significant paramagnetic character and may account for why no other diamagnetic species are observed before the hexaanion.

A hexacharged system for a relatively small carbon framework should not be entirely surprising as $\text{I}^-\text{C}_6$ bears six charges over 30 carbon atoms, that is, five carbon atoms per unit charge, precisely as in the corannulene tetraaniion (four charges over a $\text{C}_{20}$ skeleton). Nevertheless, $\text{I}^-\text{C}_6$ does boast a very high absolute degree of charge over a relatively small carbon skeleton and is the smallest PAH hexaanion ever observed.

Charge density calculations from $^{13}$C NMR spectroscopy show a $\kappa_6$ value for this hexaanion of about 102 ppm/e$^2$. While this value is somewhat smaller than the $\kappa_6$ values derived for other hexacharged systems with aromatic units of similar size, one must remember that reduction can induce major changes in the diatropic and/or paratropic ring currents in the molecule, and these also strongly affect the chemical shifts in such cases. $\kappa_6$ may deviate significantly from the “average” value.

The new diamagnetic species shows the same number of proton and carbon signals on charging as the neutral compound (four and ten respectively), with a 1:1:1:1 ratio (four and ten respectively), with a 1:1:1:1 ratio among the proton signals. No lowering of symmetry in the neutral system is seen on charging, no dimerization or aggregation is retained. On reduction, substantial upfield shifts are seen for the proton and carbon signals on charging as the neutral compound (four and ten respectively), with a 1:1:1:1 ratio (four and ten respectively), with a 1:1:1:1 ratio among the proton signals. No lowering of symmetry in the neutral system is seen on charging, no dimerization or aggregation is retained. On reduction, substantial upfield shifts are seen for C-4, H-4, and C-4d (Table 1).

The signal for C-4d is shifted from 147.9 to 95.7, an upfield shift of about 52 ppm, that of H-4 shifts from highly aromatic $8.11$ ppm to nonaromatic 3.93 ppm, whereas the corresponding C-4 resonance is shifted upfield by nearly 96 ppm, from the aromatic region of 125.6 ppm to the apparently aliphatic 29.7 ppm. This indicates a charge pattern with extremely high charge density on the above positions. From the $^{13}$C NMR spectrum, one calculates nearly a full unit of charge on each of the C-4 carbon atoms, whereas each of the C-4d carbon atoms bears more than 0.5 units of negative charge. Carbon atoms 4d and 4e of the central benzene ring clearly demonstrate the charge-alternation effect (Figure 2). Such a high charge density on the C-4 positions is in fact predicted by DFT calculations at the B3LYP/6-31G* level of theory, which show that the HOMO, HOMO-1, and HOMO-2 of $\text{I}^-\text{C}_6$ and the LUMO, LUMO+1, and LUMO+2 of 1 all have very large coefficients for the C-4 positions.

A striking feature in the NMR spectrum of $\text{I}^-\text{C}_6$ is sp$^2$ coupling for C-1, C-2, and C-3 ($\text{J}_{12} = 153.3–160.7$ Hz) but sp$^3$ coupling for C-4 ($\text{J}_{12} = 124.7$ Hz). This is the site in the molecule where the chemical shifts of the carbon (29.7 ppm) and hydrogen (3.93 ppm) atoms look more like those of a tetrahedral center than of an unsaturated trigonal center. Together, these data strongly suggest that the C-4 carbon atoms have become pyramidalized in the hexaanion of this $\text{C}_{60}$H$_{12}$.

<table>
<thead>
<tr>
<th>1$^3$C NMR, neutral</th>
<th>H-1/C-1</th>
<th>H-2/C-2</th>
<th>H-3/C-3</th>
<th>C-3a</th>
<th>H-4/C-4</th>
<th>C-4a</th>
<th>C-4b</th>
<th>C-4c</th>
<th>C-4d</th>
<th>C-4e</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$C NMR, neutral</td>
<td>121.1</td>
<td>128.5</td>
<td>127.5</td>
<td>127.5</td>
<td>115.2</td>
<td>115.6</td>
<td>115.6</td>
<td>115.6</td>
<td>125.6</td>
<td>144.7</td>
</tr>
<tr>
<td>$^{13}$C NMR, charged</td>
<td>109.3</td>
<td>114.1</td>
<td>114.1</td>
<td>121.1</td>
<td>121.1</td>
<td>121.1</td>
<td>121.1</td>
<td>121.1</td>
<td>121.1</td>
<td>139.7</td>
</tr>
<tr>
<td>$\Delta\delta(13C)$</td>
<td>−11.8</td>
<td>−10.3</td>
<td>−19.4</td>
<td>−19.4</td>
<td>−19.4</td>
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<td>−19.4</td>
</tr>
<tr>
<td>$^1$H NMR, neutral</td>
<td>7.83</td>
<td>7.46</td>
<td>7.46</td>
<td>7.46</td>
<td>7.46</td>
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</tr>
<tr>
<td>$\Delta\delta(1H)$</td>
<td>−1.27</td>
<td>−1.18</td>
<td>−2.01</td>
<td>−2.01</td>
<td>−2.01</td>
<td>−2.01</td>
<td>−2.01</td>
<td>−2.01</td>
<td>−2.01</td>
<td>−2.01</td>
</tr>
</tbody>
</table>

Charge on C$^{2+}$ | −0.115 | −0.101 | −0.190 | −0.306 | −0.937 | 0.038 | −0.139 | 0.168 | −0.510 | −0.179 |

Table 1: Experimental $^1$H NMR and $^{13}$C NMR shifts for 1 and $\text{I}^-\text{C}_6$.

$^a$ 400.1 and 100.6 MHz ($^1$H and $^{13}$C NMR, respectively), [D$_8$]THF, 220 K and 270 K for 1 and $\text{I}^-\text{C}_6$, respectively. $^b$ Neutral: $\text{J}_{12} = 7.1$, $\text{J}_{13} = 8.1$ Hz; hexaanion: $\text{J}_{12} = 7.5$, $\text{J}_{13} = 7.2$ Hz.

Figure 2. Charge distribution in tetramer of $\text{I}^-\text{C}_6$, calculated from $^{13}$C NMR shifts. Filled circles represent negative charge, and empty circles positive charge.
We considered the possibility that the main factor affecting the C–H coupling is not pyramidalization but rather the presence of an electropositive substituent at this carbon atom (e.g., methyl lithium: $J_{\text{CH}} \approx 98$ Hz vs. methyl chloride: $J_{\text{CH}} \approx 159$ Hz). However, the small $J_{\text{CH}}$ in MeLi derived, at least in part, from a concentration of $s$-orbital character in the carbon orbital pointing towards the electropositive Li center. This reduces the $s$-orbital character of the C–H bonds, which in turn reduces $J_{\text{CH}}$. The rehybridization effect in MeLi is manifested in the strongly contracted H-C-H bond angles (102.3°),[38] which signify amplified pyramidalization at this carbon atom. In light of the $J_{\text{CH}}$ data for $^{13}$C, therefore, it is difficult to avoid the conclusion that the C-4 carbon atoms must have become pyramidalized.

We were initially puzzled by the fact that calculations on bare $^{13}$C at the B3LYP/6-31G* level of theory, with no potassium ions anywhere, show no pyramidalization at any CH site on the rim. The bowl is only slightly flatter than the neutral hydrocarbon, but the C–H bonds do not bend out of the plane defined by the nearest CCC units. Calculations at the same level of theory on [[^13]C–3K]+ with potassium ions “covalently attached” at the three C-4 carbon atoms likewise show no significant pyramidalization at these sites. The potassium ions sit rather far from the carbon atoms, and the C–H bonds do not bend out of plane. From these calculations, it can be inferred that pyramidalization in the hexaanion almost certainly cannot be accounted for by a monomeric species; neither contact-ion pairing nor solvent separation perturbs the planarity of the trigonal carbon atoms. Pyramidalization must therefore be a consequence of some external influence, such as aggregation, in which potassium atoms serve as bridges between hexaanionic units. If the hexaanions do aggregate, however, each unit must be incorporated in the same way relative to the others, so that no new sets of signals are generated in the NMR spectra.

Evidence for aggregation stems not only from the anomalous $J_{\text{CH}}$ coupling constants but also from the failure of the observed NMR chemical shifts to resemble those expected for a monomeric species. An NMR-GIAO calculation at the B3LYP/6-31G(d) level of theory[33–35,39] on the monomeric hexaanion $^{13}$C with a potassium counterion “covalently attached” (exo) at each of the three C-4 positions predicts $^1$H NMR shifts of $\delta = 5.08$ (H-1), 4.68 (H-2), 5.44 (H-3), and 6.47 ppm (H-4), and $^{13}$C NMR shifts of $\delta = 118$ (C-1), 123 (C-2), 127 (C-3), 151 (C-3a), 113 (C-4), 144 (C-4a), 145 (C-4b), 148 (C-4c), 140 (C-4d), and 144 ppm (C-4e). These shifts bear little resemblance to those observed, especially at position 4 (calcld: C-4 113, H-4 6.47; obsd: C-4 29.7, H-4 3.93).

NMR-GIAO calculations on the naked hexaanion with no potassium counterions deviate even more from the observed NMR data. Clearly, the NMR spectrum of the observed hexaanion is strongly perturbed by its environment, and the species observed cannot be the simple monomeric hexaanion.

Constructing a concave-concave dimer in which three potassium atoms bridge from the C-4 carbon atoms of one bowl to those of the other yields a complex that is far too crowded to be realistic. A trimer is not possible on graph-theoretical grounds[40] (three bridges emanating from each unit requires an even number of units), but a tetrameric aggregate nicely explains the pyramidalization phenomenon observed in the NMR spectrum. A complex with all concave surfaces facing inward still creates too much crowding, but all concave surfaces facing outward accommodates the experimental results very well (Figure 3). Each potassium cation bonds two hexaanionic units together in a manner that causes the C-4 atoms to pyramidalize. Only in such an aggregate would one expect to find pyramidalization.

Note that the data do not exclude the possibility that the observed aggregate could be an even more spectacular superstructure, such as an octamer (cube) or 20-mer (dodecahedron), which are also in agreement with the observed symmetry. However, the tetramer (Figure 3) is the simplest possible structure and should be kinetically more accessible than higher order aggregates (see below).

This picture actually suggests why reduction with potassium yields the hexaanion, whereas reduction with lithium does not: the shorter C–Li distances would draw the bowls much closer together, which is disfavored on both Coulombic and steric grounds. It is also easy to understand from this picture why no intermolecular nuclear Overhauser effects (nOe) are observed; the ionic radius of K+ is quite large, and since nOe correlates to $r^2$, one would not expect to see these effects. While six potassium ions are covalently attached (or at least with strong contact-ion character),[41,42] the additional eighteen potassium ions that are not part of the cage are solvent-separated. This structure may also explain why reduction takes so long to give a clean NMR spectrum: the self-assembly process is a slow kinetic phenomenon, and it takes several weeks for the system to sort through all the aggregates and find one that is thermodynamically stable.[43]

Prolonged exposure of $^{13}$C to potassium at room temperature yields additional signals alongside those of the original aggregate. These correspond to at least four more sets of signals, in a 1:1:1:1 ratio, and with the same symmetry, but at much lower intensity than the original signals. Each set of signals falls extremely close to the original (Figure 1c), and it therefore appears that one or more additional modes of aggregation occur over time. These slowly formed aggregates of $^{13}$C are stable, as is the original tetramer,[23] and once they are formed, reestablishing the tetrameric $^{13}$C alone from them is not possible, even at higher temperatures. Thus, the first aggregate of $^{13}$C observed, although it is the kinetically

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**Figure 3.** Front and rear views of the proposed tetrameric [[^13]C–3K]+/24K+ complex (red K+, yellow H, blue C). The 18 solvent-separated K+ ions are not shown.
favored species, is not necessarily the thermodynamically most stable aggregate. Quenching this mixture with water or iodine does not lead to an isolable product, as it did with the tetramer \([1^-]_2/24\text{K}^+\). Only quenching of the first aggregate alone in water\(^{[29]}\) is successful.

In conclusion, experimental evidence from NMR spectroscopy and theoretical evidence from DFT calculations together are best explained by a tetrameric structure for \(1^-\), self-assembled in solution with \(\text{K}^+\) counterions and having tetrahedral symmetry. Calculations\(^{[33–35,39]}\) on the bare monoanionic hexaanion and with three potassium counterions fail to give pyramidalized carbon atoms or to reproduce the observed pattern of NMR shifts. A tetrameric aggregate, however, is in harmony with the symmetry, high charge density, and pyramidalization indicated in the spectra. Each unit in the aggregate is identical to the others, and six potassium ions of contact-ion character serve as an adhesive to simultaneously bond all four units together. Lower aggregates are expected to be more crowded and less stable than the proposed tetramer. The structure of the aggregate as a whole, with potassium cations bridging between hexaanionic units, is responsible for imposing pyramidalization at carbon atoms that should be planar in the bare hexaanion.

The combination of a specific number of hexaanionic units and the particular size of the potassium cation is apparently crucial in forming the supramolecular structure. The fact that no monomer of \(1^-\) is observed and that aggregation is achieved as soon as the hexaanionic state is formed shows, once again, that this is a typical trait of highly charged PAHs\(^{[15,17]}\). In the search for other appropriate PAHs that can self-assemble to anionic aggregates in solution, this discovery of the first polyhedral aggregate may serve as a useful guide.

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solutions into contact with the alkali metals. Returning the tubes to their upright positions stopped reductions from progressing.

Two types of quenching reactions were carried out: 1) with water and 2) with iodine. 1) Quenching with water was carried out in a glove bag under oxygen-free conditions. The tube was broken and opened in the glove bag and after removal of the reduction compartment and excess metal, the reduced compound was introduced into a vial containing distilled water. The characteristic color of the reduced species disappeared instantaneously, and the hexahydric species was formed. The solution was stirred for several minutes at room temperature and was then removed from the glove bag. The organic phase was washed with dichloromethane, and the solvent was evaporated. The product from the glove bag under oxygen-free conditions. The tube was broken and opened in the glove box under anhydrous conditions, and the reduced compound was immediately added to approximately 10 mol equiv of I2, upon which oxidation instantly occurred. The solution was stirred for 10 min at room temperature and was then removed from the glove box. Excess iodine was removed by washing with a saturated aqueous solution of sodium dithionite, and the solvent was evaporated. Quenching of 1H with iodine does not form a new, clean diamagnetic species; rather, it results in apparent polymerization.

Asymmetrical proton addition is likely, as indicated by 1H NMR spectroscopy.


Although no new diamagnetic species of 1 is seen, the corannulene does undergo its regular reduction: neutral \( \rightarrow \) radical anion \( \rightarrow \) dianion \( \rightarrow \) radical trion \( \rightarrow \) tetraion, as observed by 1H NMR spectroscopy.

Standing at room temperature for months in contact with the potassium mirror does not cause decomposition to 1H, aside from the formation of additional aggregates. See text.

Only after weeks of charging at room temperature is a new diamagnetic species formed.

Charge density and molecular orbital calculations were carried out at the DFT level of theory with the Gaussian98 program package, by employing Becke’s three-parameter hybrid density functional with the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP) and the 6-31G* basis set.[33–35]

\[ K = \text{parameter empirically shown to correlate the total change in chemical shift of the } ^{13} \text{C NMR spectrum on charging (} \Delta \sigma \text{) with the total extra charge added to the } \pi \text{ system of the molecule on charging (} \Sigma \Delta \sigma \text{), as expressed in the equation } \Sigma \Delta \sigma = K \Sigma \Delta \sigma. \]


Gaussian98 (Revision A.7): see Supporting Information.


\[ K, \text{a parameter empirically shown to correlate the total change in chemical shift of the } ^{13} \text{C NMR spectrum on charging (} \Sigma \Delta \sigma \text{) with the total extra charge added to the } \pi \text{ system of the molecule on charging (} \Sigma \Delta \sigma \text{), as expressed in the equation } \Sigma \Delta \sigma = K \Sigma \Delta \sigma. \]
