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Endohedral Alkali Metal Fullerene Complexes

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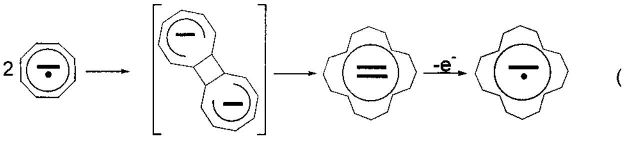
The predicted superconductivity of endohedral alkali metal fullerenes and the observed superconductivity of K_3C_{60},[1,2] coupled with their other unique magnetic and electronic properties, have prompted tremendous interest in such materials.[3,4] The high-solution electron affinities of the fullerenes[5] along with the low ionization potentials of the alkali metals would result in an electron from the alkali metal residing on the carbon cage.[3,6] Despite intense investigation, endohedral alkali metal fullerenes have not been observed, reportedly due to their extreme lability.[3,4] Patchkovskii and Thiel[7] proposed a mechanism, involving the [2 + 2] dimerization of C_{60}, for ring opening that allows the incorporation of noble gases into the C_{60} cage. Here we report the use of an analogous [2 + 2] dimerization, in the presence of alkali metal cations, to reveal the unmistakable EPR and mass spectral signatures of endohedral alkali metal ions.

In a recent article, Patchkovskii and Thiel suggest that the [2 + 2] cyclodimerization of C_{60} followed by ring opening can provide a window sufficiently large to allow the passage of noble gas atoms into C_{60}.[7] In an analogous reaction, the anion radical of cyclooctatetraene (COT), in hexamethylphosphoramide (HMPA), spontaneously dimerizes at ambient temperatures.[8−10] The [2 + 2] dimer subsequently undergoes ring opening to form the dianion and anion radical of [16]annulene, reaction 1. Since C_{60} also readily undergoes [2 + 2] cycloaddition,[11,12] it seemed reasonable that, in the presence of extra electrons, C_{60} would react with COT in HMPA to also yield a [2 + 2] cycloaddition product. Subsequent ring opening could provide a passageway to the interior of the fullerene, Figure 1.



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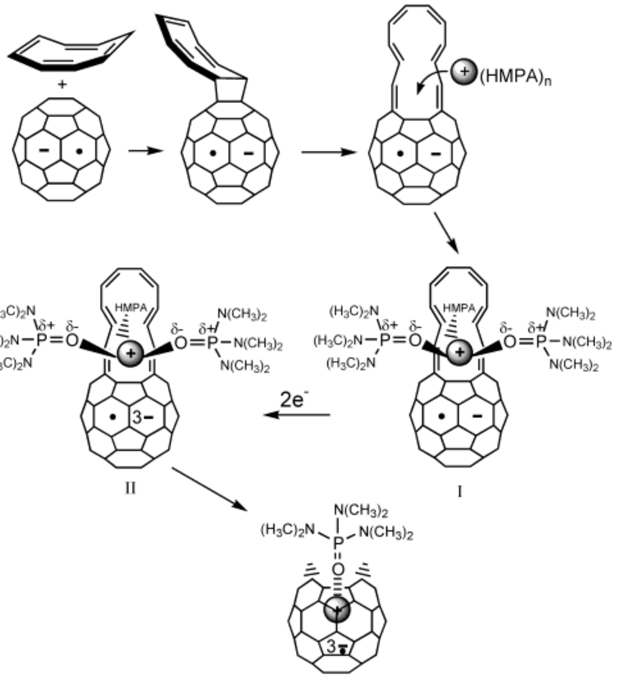

Figure 1. Proposed reaction profile leading to the incorporation of the Cs^+ ion into the $[COT-C_{60}]^{3-}$. The COT appendage is in the background and not shown in the final complex. This scheme is analogous to that shown in Figure 2 in ref 5.

The reduction (with freshly distilled alkali metal mirror in a sealed glass assembly under high vacuum) of a heterogeneous (C_{60} is insoluble in HMPA) 1:1 mixture of COT or COT-d_8 and C_{60} in HMPA with cesium metal immediately gives rise to the, previously reported,[13,14] EPR signals for $C_{60}{}^{n-}$. The $C_{60}{}^{1-}$, $C_{60}{}^{2-}$, and $C_{60}{}^{3-}$ systems are all EPR active and interconvert via disproportionation equilibria. As Cs metal is added to the COT or perdeuterated COT + C_{60} solution, the EPR signals for the anion radical and dianion of C_{60} are initially observed. After the addition of about 2 equiv of Cs, small satellite signals, two on each side of the intense signals for $C_{60}{}^{n-}$, appear (Figure 2a). These satellite signals are due to coupling to two phosphorus nuclei with $a_{^{31}P} = 13.8$ G and a single phosphorus with $a_{^{31}P} = 12.2$ G. Each of these phosphorus satellites is further split by an interaction with a single Cs nucleus ($a_{^{133}Cs} = 0.78$ G). While the Cs^+ resides in the COT appendage (gate to the fullerene, structure I in Figure 1), the Cs^+ still strongly interacts with the partially negative oxygen on three HMPA molecules. The partial positive charges on the phosphorus atoms and negative charges on the oxygen atoms set up strong Coulombic interactions with the cation and anionic portion of the complex and consequent coupling of ^{31}P atom(s) with the unpaired electron as previously observed in other systems.[15] The addition of more electrons to the fullerene increases the attraction between $C_{60}{}^{n-}$ and Cs^+ and causes the Cs^+ ions to drop further into the C_{60} cage, still attached to one molecule of HMPA (Figure 1).

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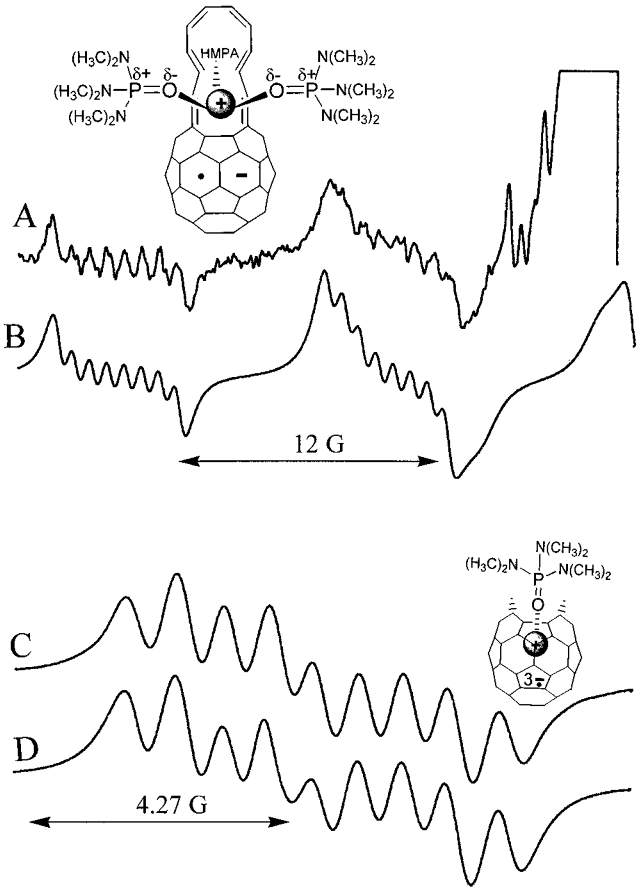

Figure 2. (A) Low field half of the EPR spectrum obtained from the addition of ca. 2 equiv of Cs metal to a 1:1 (mole:mole) mixture of perdeuterated COT and C_{60} in HMPA at ambient temperature. (B) A computer simulation of the ^{31}P satellites generated using coupling constants of 12.2 G for 2 Ps, 13.8 G for 1 P, 0.78 G for one Cs, and a line width of 0.70 G. The simulation was obtained assuming an exchange of the HMPAs at a rate of 1×10^7 s^{-1}. The large contribution from the paramagnetic C_{60}^{n-} species was not included. (C) The full (10 G scan) EPR spectrum of $[Cs@COT-C_{60}]^{\bullet 2-}$–HMPA obtained after the addition of ca. 3 equiv of Cs metal to the same solution. (D) A computer simulation generated using a single ^{133}Cs splitting of 0.725 G, a ^{31}P splitting of 0.93 G, and a line width of 0.55 G. A small contribution (4%, slightly shifted downfield) from residual paramagnetic C_{60}^{n-} species is included.

After more than 3 mol of Cs per mol of C_{60} are added,[16] the spectrum evolves into an octet from an $I = {}^7/_2$ cesium nucleus ($a_{^{133}Cs} = 0.725$ G), which is further split by a ^{31}P nucleus with $a_{^{31}P} = 0.93$ G. The very large decrease in the magnitude of $a_{^{31}P}$ indicates much more intimate association between the C_{60} cage and the Cs^+ ion accompanied by a weakening of the interaction between the Cs^+ and the oxygen on the HMPA, Figure 2. The very broad line width (0.55 G) is partially attributed to the unresolved splittings from the carbon-13 nuclei. There are 60 nonequivalent carbons that are in proximity of the Cs^+.

The predominate species is reported to be $C_{60}^{\bullet 3-}$ when C_{60} is reduced with 3 equiv of metal.[16] $C_{60}^{\bullet 3-}$ yields an almost identical EPR spectrum to that of $C_{60}^{\bullet 1-}$.[14,17] In the present case, the alkali metal ion is strongly interacting with the odd electron. Water was added to samples exhibiting the EPR signal shown in Figure 2C. Titration of these samples to a neutral end-point, as previously described, requires 3 mol of HCl per mol of C_{60}. Hence, the Cs^+ resides predominately in a $COT-C_{60}^{\bullet 3-}$ complex. This complex is a formal endohedral dianion radical. The two external alkali metal ions are HMPA solvated. In the case of cesium, the structure of this EPR active material is most appropriately written as follows: $[Cs@COT-C_{60}]^{\bullet 2-} + 2Cs^+_{(HMPA)}$.

Analogous experiments reveal much smaller K hyperfine splittings, presumably due to the smaller gyromagnetic ratio of ^{39}K. The addition of water to the HMPA solution containing the $K@C_{60}-COT^{n-}$ complex yields a brown intractable material. The solids were collected via filtration and were extracted with toluene for 24 h in a Soxhlet. Matrix-assisted laser desorption/ionization (MALDI) mass spectroscopy of the water-quenched solution reveals peaks at each mass to charge unit from 720 to 727. These represent the parent (P) and P + 1 peaks of the Birch reduction products of C_{60}^{1-}, C_{60}^{2-}, and C_{60}^{3-}. Peaks corresponding to the Birch reduction product ions of $COT-C_{60}^{n-}$ ($n = 1-3$) are also observed at 824 to 831 mass to charge units. $K@C_{60}$ is expected to be very labile.[4] Hence, we were surprised by the clear signals in the 863 to 870 region due to $K@COT-C_{60}H_x$.

The experiments reported here suggest that a host of endohedral alkali metal and alkaline earth metal fullerenes may be made available by making use of [2 + 2] cycloaddition followed by the described ring-opening mechanism.

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Supporting Information Available: MALDI mass spectrum of a toluene extract from a potassium (a much better S/N is obtained with the cesium system) reduction of C_{60} + COT in HMPA (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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