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$[C_{60}(CN)_5]^-$: A Remarkably Stable [60]Fullerene Anion

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Reaction of $C_{60}Cl_6$ with organic cyanide yielded an ionic salt comprising the fullerene anion $[C_{60}(CN)_5]^-$. This anion showed unprecedented stability in air and in solutions in the presence of water, organic and inorganic acids, and various electrophiles. The remarkable stability of the $[C_{60}(CN)_5]^-$ anion opens wide opportunities for the design of various air-stable salts incorporating different cations (metallocene, tetrathiafulvalene, and etc.) that might reveal valuable magnetic or electronic properties and find wide application in the field of material science.

Introduction

Ionic salts incorporating anions formed from pristine C_{60} have shown exciting electrical (conductivity and even superconductivity) and magnetic (ferromagnetism) properties.[1,2] However, these systems are hardly applicable as materials, as they undergo immediate degradation in air, reacting with oxygen and moisture.[3] To overcome this problem, some chemical derivatization should be carried out on the fullerene sphere to enhance its electron-accepting ability and thus to make the formation of air-stable fullerene anions possible. The design of fullerene derivatives with improved electron-accepting ability has been a challenge for fullerene chemists for more than 10 years.[4] As early as in 1995, dicyanofullerene was synthesized and it was shown that this compound is a stronger electron acceptor than C_{60}.[5] In particular, the first reduction potential of $C_{60}(CN)_2$ was measured to be ca. 120 mV more positive than that of pristine fullerene. A couple of years later, fullerene C_{60} was shown to give cyclopentadienyl-type $C_{60}Ph_5^-$ and $C_{60}Flu_5^-$ (Flu = 9-fluorenyl) anions that, however, were not stable enough in air.[6] Subsequent extensive research resulted in the preparation of numerous fullerene derivatives modified with electron-withdrawing halogen atoms or trifluoromethyl groups.[7] Some of the designed trifluoromethylated fullerenes were much stronger electron acceptors than the parent fullerene. For example, the reduction potential of one of the isolated isomers of $C_{60}(CF_3)_{10}$ was more than 0.5 V more positive than that of virgin C_{60}.[8] Virtually all known trifluoromethyl derivatives of fullerenes were isolated on the scale of a few milligram from complicated crude product mixtures by using HPLC. Perhaps this is a reason why the formation of any air-stable anions from these compounds was not achieved up to date.

Summarizing available literature data, we can conclude that attachment of cyano groups is the most efficient route for the enhancing electron-accepting power of the fullerene cage. Previously reported synthesis of $C_{60}(CN)_2$ was achieved by using nucleophilic addition of cyanide anion to the fullerene molecule followed by quenching of the formed anion $[C_{60}CN]^-$ with tosyl cyanide.[5] However, the addition of cyanide anions to more than one double bond on the fullerene cage showed poor selectivity and yielded complicated mixtures of isomeric products.[9] Therefore, we suggested an alternative procedure that is based on a nucleophilic substitution of halogen atoms in readily available halofullerenes with cyanide. Here we report a facile conversion of chlorofullerene $C_{60}Cl_6$ into the first air-stable fullerene anion $[C_{60}(CN)_5]^-$.

Results and Discussion

Our preliminary experiments showed that treatment of $C_{60}Cl_6$ with KCN under various conditions results in the precipitation of a dark solid possessing the composition $K^+[C_{60}(CN)_5]^-$ as determined by chemical analysis. However, no spectroscopic or crystallographic characterization of this product was possible at that time. As a next step, we applied organic cyanide $Et_4N^+CN^-$ as a reagent for cyanation of $C_{60}Cl_6$. Addition of this salt to $C_{60}Cl_6$ dissolved in

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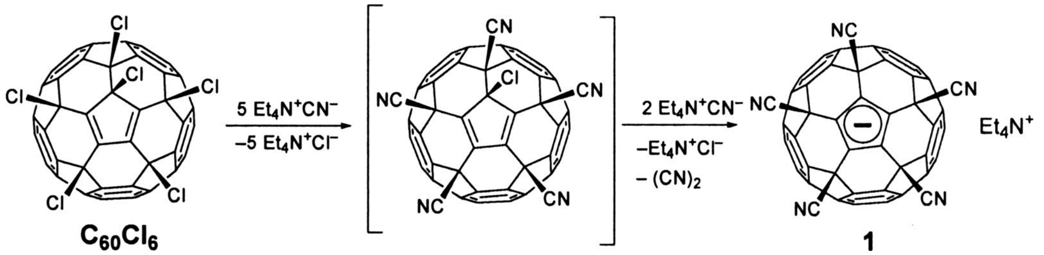

Scheme 1. The proposed mechanism of transformation of $C_{60}Cl_6$ into **1**.

chlorobenzene or 1,2-dichlorobenzene resulted in immediate color change from bright red ($C_{60}Cl_6$) to dark brown. Conversion of $C_{60}Cl_6$ into some highly polar products was very fast (5 min) and almost quantitative as follows from TLC examination. To ensure completion of the reaction, the reagents were stirred at room temperature for the next few hours. Subsequent column chromatography separation of the crude product on silica by using toluene/acetonitrile mixtures as eluent yielded few distinct fractions. A major fraction contained a single component that was revealed to be $Et_4N^+[C_{60}(CN)_5]^-$ (**1**) formed in 40–50% yield. Molecular compositions and structures of a few byproducts formed in this reaction are under investigation now.

The formation of salt **1** from $C_{60}Cl_6$ can be rationalized as follows. Initially, five outlining chlorine atoms are replaced nucleophilically with cyano groups (most probably via S_N1 mechanism). Such reaction pathway is well established for chlorofullerene $C_{60}Cl_6$.[10] Afterwards, the proposed intermediate $C_{60}(CN)_5Cl$ undergoes rapid two-electron reduction by cyanide anion with the formation of $[C_{60}(CN)_5]^-$ and dicyan $(CN)_2$ as a byproduct. Reduction of fullerene C_{60} with cyanine anion has been described,[5] as has the two-electron reduction of $C_{60}Ph_5Cl$ with the formation of anion $C_{60}Ph_5^-$.[11] The conjectured mechanism of the transformation of $C_{60}Cl_6$ into **1** is shown in Scheme 1.

The composition of **1** was revealed by ESI mass spectrometry. The negative-ion mass spectrum of **1** showed a single peak at $m/z = 850$ attributed to the $[C_{60}(CN)_5]^-$ anion (Figure 1). The positive-ion mass spectrum showed a signal due to the organic cation.

A remarkably simple ^{13}C NMR spectrum should correspond to the highly symmetrical C_{5v} structure of the $[C_{60}(CN)_5]^-$ anion. The low-field part of the spectrum should comprise seven resonances due to the sp^2 carbon atoms of the fullerene cage and one resonance due to the CN group.

Indeed, the experimentally obtained ^{13}C NMR spectrum of **1** exhibited only eight lines in the 110–150 ppm region that fit perfectly to the spectrum expected for the $[C_{60}(CN)_5]^-$ anion. The high-field part of the spectrum comprised a set of signals due to the Et_4N^+ cation and a very low intensive peak attributed to the sp^3 carbon atom of the fullerene cage.

The CN group resonance and one of the sp^2 carbon atoms of the fullerene cage appeared at 116–118 ppm (peaks 7 and 8 in Figure 2) so that it was not possible to assign each of them precisely. The rest of the peaks corresponded to the sp^2 carbon atoms of the fullerene cage. We note here that very similar spectra were observed previously for the $C_{60}Ph_5^-$ and $C_{60}Flu_5^-$ anions.[7] Thus, a small number of signals in the experimentally obtained ^{13}C NMR spectrum and its similarity with the previously reported data for cyclopentadienyl-type fullerene anions corroborate strongly the highly symmetrical molecular structure of **1** suggested here.

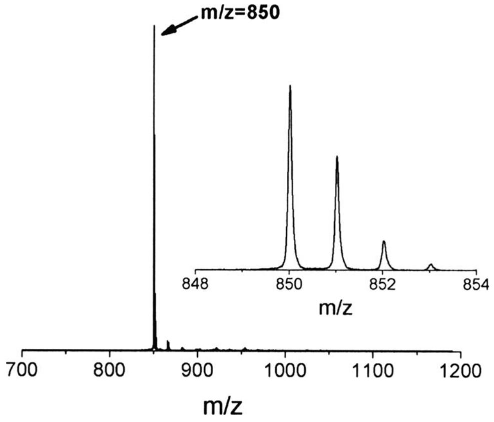

Figure 1. ESI mass spectrum of **1**. Inset shows focus on the m/z = 850 amu peak due to $[C_{60}(CN)_5]^-$.

The IR spectrum of **1** was quite similar to the spectrum of the parent $C_{60}Cl_6$ especially in the regions 400–550 cm^{-1} and 1300–1500 cm^{-1} where the fullerene cage carbon–carbon bond vibrations appear (Figure 3).

It might be also considered that a set of the signals due to the C–Cl vibrations at 580–950 cm^{-1} in the spectrum of $C_{60}Cl_6$ resemble somehow a set of the bands due to the C–CN vibrations at 990–1250 cm^{-1} in the spectrum of **1**. The sharp band due to the C≡N vibrations appeared at 2236 cm^{-1} in the spectrum of **1**. The absorption spectrum of **1** has no sharp features and resembles the spectrum of the precursor chlorofullerene (Figure 4). The similarity of the IR and absorption spectra of $C_{60}Cl_6$ and those of the salts of the $[C_{60}(CN)_5]^-$ anion might be a consequence of the similar addend distributions on the fullerene cages of these species.

Thus, the obtained spectroscopic data proved unambiguously that the $[C_{60}(CN)_5]^-$ ion indeed has the highly symmetrical C_{5v} structure shown in Scheme 1. The negative charge in this ion is distributed over the cyclopentadienyl ring embedded in the fullerene cage like in the case of the previously obtained $C_{60}Ph_5^-$ and $C_{60}Flu_5^-$ anions. More-

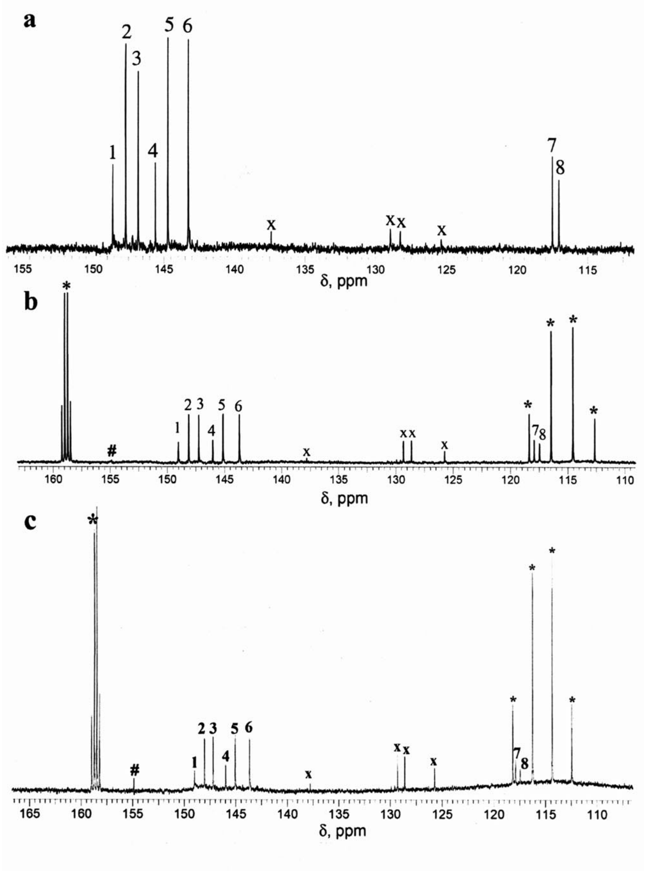

Figure 2. Low-field part of the ^{13}C NMR spectrum of **1** in pure $[D_6]DMSO$ (a); spectra of the same sample after addition of ca. 200 equiv. of CF_3COOH (b) and following addition of ca. 500 equiv. of 33% DCl in D_2O (c). Peaks due to the $C_{60}[CN]_5^-$ anion are labeled with numbers 1–8; symbol "*" denotes peaks of CF_3COOH; symbol "x" is due to an impurity of toluene, symbol "#" marks a peak due to some pollution present in the added drops of CF_3COOH.

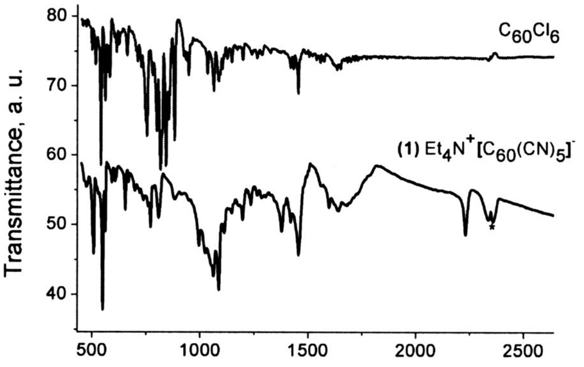

Figure 3. IR spectra of **1** and parent $C_{60}Cl_6$. Symbol "*" denotes noncompensated vibrations of atmospheric CO_2.

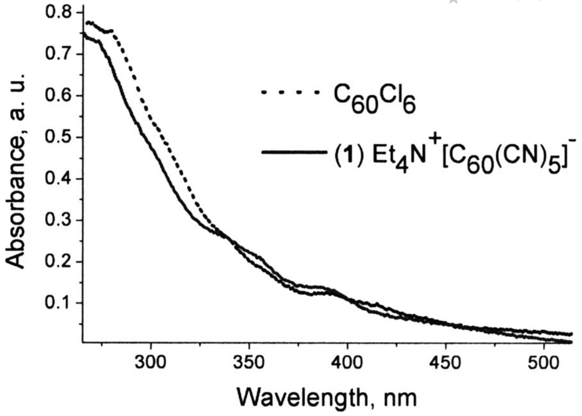

Figure 4. Absorption spectra of **1** and parent $C_{60}Cl_6$.

over, a strong field-effect of five electron-withdrawing CN groups stabilizes additionally the negative charge delocalized in the cyclopentadienyl ring. Owing to such great stabilization, the $[C_{60}(CN)_5]^-$ anion demonstrated a remarkable stability. First, no signs of degradation were observed when samples of **1** were stored in air for few months, which proves the environmental stability of the fullerene anion. Second, our attempts to quench the $[C_{60}(CN)_5]^-$ anion with electrophiles were unsuccessful. For instance, treatment of **1** with molecular iodine as well as heating at reflux with methyl iodide for 10 h resulted in quantitative recovery of the starting material.

These results suggest that the $[C_{60}(CN)_5]^-$ anion has an unusually high oxidation potential. Indeed, our preliminary cyclic voltammetry (CV) measurements in DMF showed that $[C_{60}(CN)_5]^-$ can be oxidized only at potentials as high as +0.71 V vs. Fc/Fc^+.* We note that this value is just ca. 0.6 V lower than the oxidation potential of the parent C_{60}, which is a neutral molecule.[12] At the same time, the oxidation potential of $[C_{60}(CN)_5]^-$ is ca. 1.1 V more positive than that of the $C_{60}Ph_5^-$ anion reported previously.[13] Such a great difference between the oxidation potentials of these two anions reflects the strong electron-withdrawing effect of five cyano groups surrounding the cyclopentadienyl ring and the stabilizing negative charge in $[C_{60}(CN)_5]^-$. It is notable that the oxidation of **1** is irreversible. This can be explained by the very high reactivity of the $[C_{60}(CN)_5]^{\cdot}$ radical formed upon oxidation of the anion. This radical might be rapidly quenched by a solvent, it might recombine with the formation of the $[C_{60}(CN)_5]_2$ dimer, or it might undergo another kind of degradation. We note also that $[C_{60}(CN)_5]^-$ can be further reduced with the formation of the $[C_{60}(CN)_5]^{2-}$ dianion at a potential of –1.24 V, which is close to the second reduction potential of $C_{60}(CN)_2$, corresponding to –1.33 V. Additional and more comprehensive studies of the electrochemistry of **1** are in progress at the moment.

Chemical and electrochemical oxidation experiments point to the remarkable stability of the $C_{60}[CN]_5^-$ anion. We investigated further a possibility to protonate this anion to form the corresponding C–H acid $C_{60}(CN)_5H$ (**2**). For this purpose, we added some strong acids to **1** dissolved in $[D_6]DMSO$ directly in the NMR tube. In the first experiment, a few drops of trifluoroacetic acid were added to the sample. The ^{13}C NMR spectrum obtained from this mixture showed the same set of the signals due to the $[C_{60}(CN)_5]^-$ anion together with resonances of the trifluoroacetic acid and toluene impurity (Figure 2b). This remarkable result shows that $[C_{60}(CN)_5]^-$ is stable in the presence of trifluoroacetic acid and does not undergo protonation. In other words, $C_{60}(CN)_5H$ (**2**) is a stronger acid than CF_3COOH, which has a pK_a of 0.23. As a next step, we added a few drops of 33% DCl dissolved in D_2O to the NMR tube with a solution of **1** in DMSO/CF_3COOH. The following acquisition of the ^{13}C NMR spectrum revealed all signals of the $[C_{60}(CN)_5]^-$ anion (Figure 2c). Thus, the anion was not protonated even by such a strong inorganic acid as DCl and the parent acid $C_{60}(CN)_5H$ was not formed.

On the one hand, these results make evident that $C_{60}(CN)_5H$ has a pK_a lower than –7.0 and represents one of the strongest C–H acids known in organic chemistry. On the other hand, the conducted experiments prove the unprecedented stability of the $[C_{60}(CN)_5]^-$ anion and its salts.

Conclusions

The results reported in this manuscript open wide opportunities for the design of numerous air-stable salts incorporating $[C_{60}(CN)_5]^-$ anions. Such ionic compounds might be useful in many material science applications.[14] Moreover, new members of the family of stable cyanofullerene anions might become available in the near feature. In particular, we have already observed the air-stable fullerene dianions $[C_{60}(CN)_8(OH)_2]^{2-}$, $[C_{60}(CN)_9(OH)]^{2-}$, and $[C_{60}(CN)_{10}]^{2-}$ by ESI MS (see Supporting Information) and work now on their isolation and spectroscopic characterization.

Experimental Section

Precursor chlorofullerene $C_{60}Cl_6$ (100 mg, 0.11 mmol) prepared as described earlier[15,16] was dissolved in chlorobenzene (100 mL). A solution of organic cyanide $Et_4N^+CN^-$ (230 mg, 0.88 mmol) in chlorobenzene (10 mL) was added dropwise within a period of 5–10 min. The resulting dark brown mixture was stirred for the next 2 h to ensure completion of the reaction. Afterwards, the mixture was filtered, and the filtrate was poured on top of a silica gel column (40–60 µm, 60 Å) washed in advance with toluene. Elution with toluene/acetonitrile mixtures with component ratios varying from 99:1 to 50:50 yielded three distinct fractions. A dark brown material eluted with the first fraction (a major one) was analyzed as **1** (yield 47 mg, 45%). ^1H NMR (600 MHz, [D$_6$]DMSO): δ = 1.18 (t, 12 H, CH_3), 3.08 (m, 8 H, CH_2) ppm. ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 9.00 (CH_3), 46.15 (CH_2), 68.71 (cage sp^3 C), 122.23, 122.69, 148.45, 149.90, 150.78, 152.00, 152.88, 153.79 ppm. MS (ESI–): m/z = 850.019 $[C_{60}(CN)_5]^-$. IR (KBr pellet): $\tilde{\nu}$ = 506.5, 549, 561, 590.5, 606.5, 653.5, 771, 808, 883.5, 995, 1023.5, 1062, 1087, 1112.5, 1197.5, 1378.5, 1420, 1456, 1598, 1640.5, 1682, 2231.5, 2849.5, 2918.5, 2956 cm^{-1}. $C_{73}H_{20}N_6$ (981.0): calcd. C 89.38, H 2.05, N 8.57; found C 89.13, H 2.39, N 8.41.

Supporting Information (see footnote on the first page of this article) Graphs with the ^1H and 2D H–H COSY, H–C HSQC, H–C HMBC NMR spectra of **1**; ESI mass spectrum demonstrating distinct peaks due to $[C_{60}(CN)_9(OH)]^{2-}$, $[C_{60}(CN)_8(OH)_2]^{2-}$, and $[C_{60}(CN)_7(OH)_3]^{2-}$ dianions.

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