Fullerenes

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Saturnene Revealed: X-ray Crystal Structure of D_{5d}-$C_{60}F_{20}$ Formed in Reactions of C_{60} with A_xMF_y Fluorinating Agents (A = Alkali Metal; M = 3d Metal)**

Natalia B. Shustova, Zoran Mazej, Yu-Sheng Chen, Alexey A. Popov, Steven H. Strauss, and Olga V. Boltalina**

New fluorinated carbon materials (FCMs) have been[1] and continue to be prepared and studied because of their extant or potential applications in energy storage, low-surface-energy coatings, low-dielectric materials, bioengineering, medicine, and lubrication.[2–6] One class of FCMs, fluorofullerenes (FFs), are known to have variable optical gaps[7] and have been used as dopants to improve the surface conductivity of diamond[8] and as components of LED devices.[9] One attractive feature of FFs that distinguishes them from most other FCMs is that they are molecular and in many cases have been isolated with 85 mol% purity or higher as single isomers with well-determined structures and well-determined, reproducible physicochemical properties.[10] These FFs include 13 $C_{60}F_n$ compounds ($n = 2$, 4, 6, 8 (two isomers), 18, 20, 24, 36 (three isomers), 38, 48) and several dozen fluorinated higher fullerenes and heterofullerenes.[10]

For any FF to become a practical component of an FCM for a particular application, its efficient synthesis and purification must be possible. However, selective syntheses, defined as reactions that produce at least 85 mol% of a single composition in the crude product mixture, are known for only three $C_{60}F_n$ compositions, $C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}F_{48}$,[11–13] and only two of them, $C_{60}F_{18}$ and $C_{60}F_{48}$, are produced as single isomers. We now report new reactions of C_{60} with a variety of ternary metal fluorides A_xMF_y, in which A is an alkali metal and M is a high-valent 3d metal. Among the reactions reported is a selective synthesis of the composition $C_{60}F_{44}$. We also report a nonchromatographic purification of the previously reported FF $C_{60}F_{20}$.[14] This alternative technique enabled us to verify the proposed Saturn-like structure of this compound by X-ray crystallography.

The use of d-block metal fluorides as fluorinating agents (FAs) for the synthesis of FFs was first reported in 1995.[15] In general, these FAs are softer, more selective, and safer to use than F_2, XeF_2, or KrF_2.[10] For example, the degree of fluorination (i.e., the value of n in the $C_{60}F_n$ products) can be controlled by varying the oxidation state of the metal or by "adding" alkali metal fluorides (i.e., by using a mechanical mixture of AF and MF_x or a ternary salt A_xMF_y).[16]

We carried out the reactions of C_{60} and the FAs MF_x or A_xMF_y listed in Table 1. Most of these FAs were used for fullerene fluorination for the first time (the exceptions are CoF_3[12] and MnF_3, $KMnF_4$, and K_3MnF_6[16]). The FAs can be roughly divided into two groups: those which produced $C_{60}F_n$ FFs with I) $n > 36$ and II) $n \leq 36$. The first group includes ternary metal fluorides containing Cr^{V}, Ni^{IV}, and Cu^{IV}. These high-oxidation-state compounds produced FFs with $n = 42$, 44, and 46. In the case of Cs_2CuF_6 under the reaction conditions indicated, the composition $C_{60}F_{44}$ was synthesized selectively. The ^{19}F NMR spectrum of the reaction mixture showed that several $C_{60}F_{44}$ isomers were probably present. In ongoing studies, we are attempting to develop selective syntheses for $n = 42$, 44, and 46 with these FAs and to separate the isomers produced by using all available means.

The second group of FAs includes ternary salts containing Mn^{III} and Co^{III}. It is known that CoF_3 is a more active FA than MnF_3.[16–18] In the present study, this difference is manifested in the FF products of C_{60} fluorination under identical conditions: $C_{60}F_{36}$ was formed primarily along with small amounts of $C_{60}F_{18}$ and $C_{60}F_{20}$ when MnF_3 was used, and $C_{60}F_{38}$ and $C_{60}F_{40}$ were formed primarily along with some $C_{60}F_{36}$ when CoF_3 was used. It was also found that $LiCoF_4$ is a stronger FA than $LiMnF_4$. However, neither K_3CoF_6 nor K_3MnF_6 produced any FFs, so their relative fluorinating abilities for C_{60} cannot be compared.

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[*] N. B. Shustova, Prof. S. H. Strauss, Dr. O. V. Boltalina
Department of Chemistry, Colorado State University
Fort Collins, CO 80523 (USA)
Fax: (+1) 970-491-1801
E-mail: steven.strauss@colostate.edu
olga.boltalina@colostate.edu

Dr. Z. Mazej
Department of Inorganic Chemistry and Technology
Jožef Stefan Institute, 1000 Ljubljana (Slovenia)

Dr. Y.-S. Chen
ChemMatCARS, Center for Advanced Radiation Sources
The University of Chicago
c/o Advanced Photon Source/Argonne National Laboratory
Argonne, IL 60439 (USA)

Dr. A. A. Popov
Department of Electrochemistry and Conducting Polymers
Leibniz Institute for Solid State and Materials Research
01069 Dresden (Germany)

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Table 1: Fluorinating agents, reaction conditions, and products of C_{60} fluorination.[a]

FA	FA/C_{60}	T [°C]	t [h]	Major products,[b] n in $C_{60}F_n$	Minor products,[b,c] n in $C_{60}F_n$
$KCrF_6$	46:1	270	6.5	46, 44	42, 48
$RbCrF_6$	46:1	270	4	46, 44	42, 48
$CsCrF_6$	46:1	270	10	44, 46	42, 48
MnF_3	40:1	420	10	36	18, 20
$LiMnF_4$	10:1	470	3	18	2–8, 20
$LiMnF_4$	20:1	470	3.5	18, 36	2–8, 20
$LiMnF_4$	30:1	470	10	36, 18	2–8
$LiMnF_4$	40:1	470	3.5	36, 18	
$KMnF_4$	40:1	470	3.5	36, 18	2–8, 20
$CsMnF_4$	10:1	470	3	no FFs	
K_3MnF_6[d]	40:1	470	3.5	no FFs	
CoF_3	40:1	420	10	38, 40	36
$LiCoF_4$	40:1	432	8.5	36, 38	
$LiCoF_4$	15:1	480	7	36, 18	2–8, 20
$LiCoF_4$	40:1	480	7	36, 38	
K_3CoF_6	15:1	480	7	no FFs	
K_3CoF_6	40:1	480	7	no FFs	
K_2NiF_6	46:1	380	10	44	46, 42
Cs_2CuF_6	50:1	330	10	44	42

[a] All data were obtained in this study, unless otherwise indicated. [b] The more abundant product is listed first; product ratios were determined by APCI mass spectrometry. [c] $n = 2$–8 includes $n = 2$, 4, 6, and 8. [d] Data from Ref. [16].

Efficient syntheses of $C_{60}F_n$ FFs with $n \leq 20$ have proven difficult to develop. The products must be sublimed from the mixture of C_{60} and FA in the reactor hot zone before they accumulate more F atoms than desired, and their sublimation requires temperatures on the order of 470–500 °C (not surprisingly, FF sublimation temperatures decrease as n increases). However, C_{60} also sublimes out of the hot zone at these temperatures, which significantly lowers the conversion of C_{60} into FFs. Furthermore, although $C_{60}F_{18}$ can be prepared selectively in high yield as a single isomer,[11] the homologous composition $C_{60}F_{20}$, which is only known as a single isomer that cannot be formed by the addition of two F atoms to C_{3v}-$C_{60}F_{18}$, cannot: it has only been prepared as a minor impurity in FF syntheses.[14] Therefore, we were pleased to discover that $LiMnF_4$ is a more effective FA for the production of FFs with $n = 2$, 4, 6, 8, and 20 than most other FAs we have examined to date, although even with $LiMnF_4$ these compounds are only formed in minor amounts relative to $C_{60}F_{18}$. The results in Table 1 show that the distribution of FFs is strongly dependent on the $LiMnF_4/C_{60}$ molar ratio. For example, a change in this ratio from 40 to 10 led to a change in the $I(C_{60}F_{18})/I(C_{60}F_{36})$ ratio by a factor of 350, from 0.077 to 27 (I is the integrated HPLC peak intensity at the detector wavelength of 300 nm). The optimal conditions for the production of $C_{60}F_{2-8}$ and $C_{60}F_{20}$ were found to be: $LiMnF_4/C_{60}$ 20:1, $T = 470$ °C, $t = 3$ h. These conditions led to a low overall conversion of C_{60} (ca. 25 %) but the greatest amounts of $C_{60}F_{2-8}$ and $C_{60}F_{20}$. The milligram amounts of $C_{60}F_{20}$ prepared in these studies enabled us to determine its structure by single-crystal X-ray diffraction.

The one-line ^{19}F NMR spectrum and IR spectrum were used in conjunction with DFT calculations to propose the D_{5d} "saturnene" structure of $C_{60}F_{20}$,[14] which is shown as a Schlegel diagram in Figure 1.[14,20] The addition patterns for $C_{60}F_2$, $C_{60}F_4$, $C_{60}F_6$, the two known isomers of $C_{60}F_8$, and C_{3v}-$C_{60}F_{18}$[19] are also shown in Figure 1. All of these compounds can be purified readily by HPLC with the exception of $C_{60}F_{20}$ owing to its very long retention time (74 min if toluene is the eluent[14]). An additional complication was that the 74 min fraction required additional processing with a different HPLC column when impurities such as $C_{60}F_{12}$, $C_{60}F_{14}$, and $C_{60}F_{20}O$ were present.[20] As a result of the larger amounts of $C_{60}F_{20}$ now present in our product mixtures, we discovered a more efficient, nonchromatographic purification method for this compound: fractional crystallization (this method was previously used to purify C_3-$C_{60}F_{36}$ from a mixture of the three isomers of $C_{60}F_{36}$[21]). Slow evaporation of a benzene solution of $C_{60}F_{18}$, $C_{60}F_{36}$, and small amounts of $C_{60}F_{20}$ and $C_{60}F_{2-8}$ resulted in the formation of colorless crystals of $C_{60}F_{20}{\cdot}2\,C_6H_6$ suitable for diffraction. Despite the prediction[22] based on a polarizable continuum model at the Hartree–Fock (HF) level of theory that $C_{60}F_{20}$ should be highly soluble in nonpolar as well as polar solvents, we have found that $C_{60}F_{20}$ is the least soluble FF reported to date.

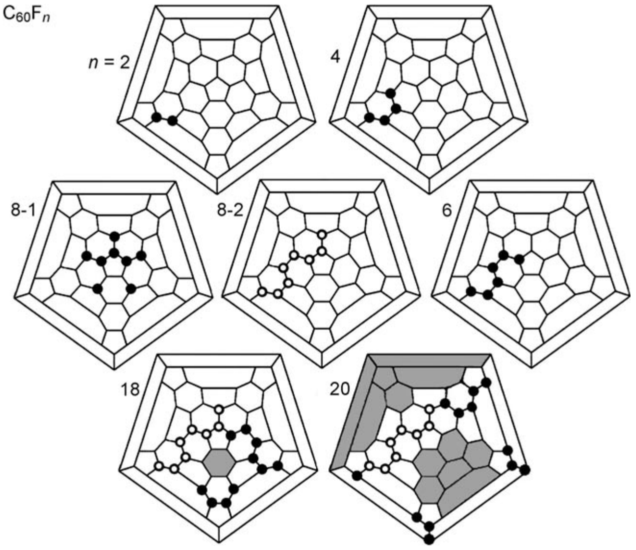

Figure 1. Schlegel diagrams of known $C_{60}F_n$ compounds with $2 \leq n \leq 20$ (two isomers are known with $n = 8$). The filled and hollow circles indicate CF vertexes. The hollow circles show the addition pattern of an isomer of $C_{60}F_8$ (8-2), which may be a common intermediate in the formation of $C_{60}F_{18}$ and $C_{60}F_{20}$.

The structure of $C_{60}F_{20}{\cdot}2\,C_6H_6$ confirms the D_{5d} saturnene structure of this FF. There are two nearly identical centrosymmetric saturnene molecules and two benzene molecules in the asymmetric unit. The structure of one of the saturnene molecules is shown in Figure 2. Other views of $C_{60}F_{20}$ are shown in the Supporting Information. The molecule is expanded by 12 % at the equator relative to the structure of C_{60}[23] as a result of the loop of $C(sp^3)$ atoms, but is compressed by only 3.8 % at the poles. The distance between the centroids of opposite 6,6-edge $C(sp^3)-C(sp^3)$ bonds in $C_{60}F_{20}$ is 7.79 Å,

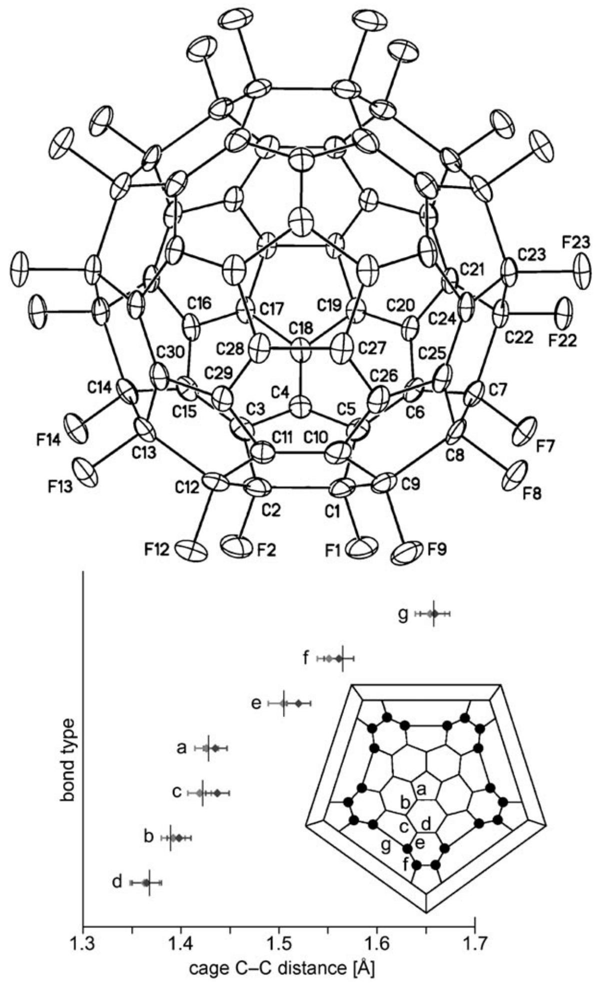

Figure 2. Structure of one of the two nearly identical $C_{60}F_{20}$ molecules (50% probability ellipsoids). Only the unique portion of the centrosymmetric molecule is labeled. The range of C–F distances over both molecules is 1.380(3)–1.396(3) Å (1.373 Å found in DFT calculations). The graph shows the distance ranges for the seven types of cage C–C bond (the error bars are $\pm 3\sigma$; the distances predicted at the B3LYP/6-311G(2d) level of theory are shown as vertical lines). These ranges are (bond type, example and distance range [Å], [DFT-predicted distance, Å]): a, C17–C18 1.426(4)–1.435(4) [1.428]; b, C4–C18 1.392(4)–1.398(4) [1.389]; c, C3–C4 1.419(4)–1.437(4) [1.422]; d, C3–C15 1.363(5)–1.365(5) [1.368]; e, C2–C3 1.504(5)–1.520(4) [1.505]; f, C2–C12 1.551(4)–1.561(5) [1.565]; g, C1–C2 1.654(5)–1.659(5) [1.658].

whereas the distance between the centroids of the corresponding C(sp^2)–C(sp^2) bonds in C_{60} is only 6.95 Å.[23] In contrast, the distances between the centroids of the polar pentagons in $C_{60}F_{20}$ and C_{60} are 6.63 and 6.39 Å, respectively. The very long type g C–C single bonds (1.654(5)–1.659(5) Å) are similar in length to those observed in D_3-$C_{60}F_{48}$ (1.627(7) Å)[24] and C_{3v}-$C_{60}F_{18}$ (1.672(4) Å)[19] but are considerably shorter than the "ultralong" C–C bonds ($\geq$ 1.75 Å) in hexaphenylethane derivatives.[25]

The two fragments of saturnene formed by type a, b, c, and d C–C bonds have the same carbon framework as corannulene, $C_{20}H_{10}$ (the type e C–C single bonds in $C_{60}F_{20}$ are analogous to the C–H bonds in $C_{20}H_{10}$). Another fullerene derivative with a Saturn-like structure, D_{5h}-$C_{50}Cl_{10}$, also has two corannulene-like fragments.[26] The X-ray crystal structure of corannulene[27] is compared with those of the corannulene-like fragments of $C_{60}F_{20}$ and $C_{50}Cl_{10}$ in the Supporting Information (the data for all three structures were collected over the relatively narrow temperature range of 90(2)–120(2) K). The C–C bond distances are similar (the ranges for the four bond types overlap with one another). Since both fullerene molecules are constrained as spheroids, and corannulene is not, the "bowls" of the corannulene-like fragments of $C_{60}F_{20}$ and $C_{50}Cl_{10}$ are deeper (ca. 1.50 Å from rim to bottom) than for corannulene itself (ca. 0.86 Å from rim to bottom).

The unit-cell packing of $C_{60}F_{20}$ can be described as idealized body-centered cubic (Figure 3). Each fullerene is surrounded by four benzene molecules, the centroids of which form almost a perfect square with sides of 9.34 and 9.41 Å and angles of 89.5 and 90.5° (the four benzene centroids are 6.20 or 6.37 Å from the fullerene centroid). The perpendicular distance between the benzene planes and the plane of the closest fullerene hexagon is 3.336 Å. The closest F⋯F distances between $C_{60}F_{20}$ molecules are 2.709(3) and 2.831(3) Å. The tight packing of the fullerene and solvent molecules is probably responsible for the very low solubility of this compound in organic solvents.

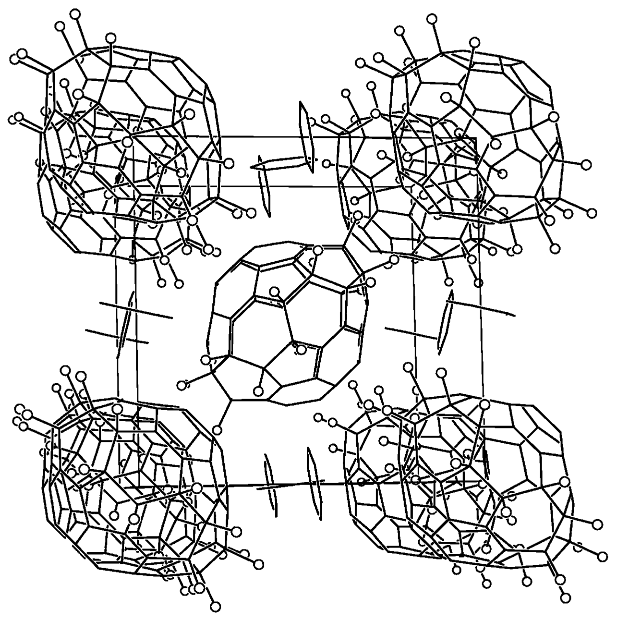

Figure 3. Packing of $C_{60}F_{20}$ and C_6H_6 molecules in $C_{60}F_{20}\cdot 2\,C_6H_6$ (H atoms are omitted for clarity; F atoms are shown as spheres of arbitrary size). The centrosymmetric triclinic unit cell, which approximates a cube, is also shown. The fluorofullerene molecules pack in an idealized body-centered-cubic array with C_6H_6 molecules centered on four of the six unit-cell faces. The fullerene centroid⋯centroid distances between the center and the corners of the cell are 11.09–11.36 Å. The centroid⋯centroid distances along the crystallographic *a* axis (perpendicular to the page) are 12.47 Å.

Experimental Section

C_{60} (99.5%, Term USA) was used as received. HPLC-grade solvents (toluene, heptanes) were used for HPLC analysis. All metal fluorides were prepared by known or modified procedures (see the Supporting

Information for details) and were handled in a glove box under an inert atmosphere. Fluorination reactions were performed in nickel reaction vessels. Instrumentation for analysis of the products included a Finnigan LCQ Duo mass spectrometer with an atmospheric pressure chemical ionization (APCI) ion source and a Shimadzu Prominence HPLC system equipped with a 10×250 mm^2 Buckyprep Cosmosil column.

Crystal data for $C_{60}F_{20}\cdot2C_6H_6$: $M_r=1256.82$ g mol^{-1}, $0.02\times0.03\times0.07$ mm^3, triclinic, $P\bar{1}$, $a=12.4647(9)$, $b=13.2404(9)$, $c=13.2742(9)$ Å, $\alpha=90.465(2)$, $\beta=90.655(2)$, $\gamma=91.403(2)°$, $V=2189.9(3)$ Å^3, $Z=2$, $\rho_{calcd}=1.906$ Mg m^{-3}, $\mu=0.061$ mm^{-1}, $\lambda=0.41328$ Å, ChemMatCARS sector 15IDB at the Advanced Photon Source at Argonne National Laboratory, $2\theta_{max}=15.17°$, $T=120(2)$ K, 50290 reflections, 9049 independent reflections ($R_{int}=0.0762$), 829 parameters, 0 restraints, full-matrix least-squares refinement on F^2, semiempirical absorption correction from equivalents, final R_1-($I>2\sigma(I)$) = 0.0548, final $wR_2=0.1304$, largest difference peak and hole 0.393 and −0.0.325 Å^{-3}. CCDC 747664 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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