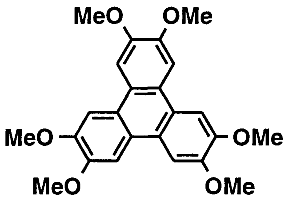
CHEMISTRY LETTERS, pp. 981-984, 1994.

Synthesis and Complex Crystal Structure of C_{60} with Symmetrical Donor of 2,3,6,7,10,11-Hexamethoxytriphenylene (HMT)

Long Y. CHIANG,[*] John W. SWIRCZEWSKI,[†] Ken LIANG,[†] and J. MILLAR[†]
Center for condensed Matter Sciences, National Taiwan University, Taipei, Taiwan
[†]Corporate Research Laboratory, Exxon Research and Engineering Company,
Annandale, New Jersey 08801, USA

We have successfully synthesized the complex of C_{60} fullerene with a three-fold symmetrical donor of 2,3,6,7,10,11-hexamethoxytriphenylene (HMT). All spectroscopic data and analyses support the chemical composition of this complex as $C_{60}(HMT)_2$. Individually, each C_{60} fullerene sphere was found to be surrounded by four HMT molecules in distinctive tetrahedral arrangement. The closest distance from one C_{60} centroid to the next C_{60} centroid in the adjacent chain is 13.099 Å.

Fullerene C_{60} molecules exhibit versatile multiple reductive electronic states1) that makes it suitable for use as a molecular acceptor in the synthesis of new solid state materials with electronic donors. Examples of charge transfer complexes comprised of C_{60} include C_{60}(TDAE),2) C_{60}-chromium(II) porphyrin,3) C_{60}-hydroquinone,4) and C_{60}-BEDT-TTF.5) Here we report the synthesis and the crystal structure study of C_{60} complex with a highly symmetrical organic donor. Recently, highly symmetrical donors have been utilized as components in organic charge-transfer complexes6-8) for the study of organic magnetism and intermolecular spin exchanges in this class of materials. One of the most thermally stable organic donors possessing degenerated HOMO orbitals is 2,3,6,7,10,11-hexamethoxytriphenylene (HMT, **1**).6) The triplet e.s.r. resonance corresponding to the dicationic HMT^{+2} was observed to be stable from 5 K to ambient temperature in complex solid state.9) Complexation reaction between HMT and C_{60} fullerene is therefore our interest aimed to investigate solid state properties of the resulting product as well as the intermolecular spin interactions between C_{60} and HMT moieties.



1, **HMT**

Synthesis of 2,3,6,7,10,11-hexamethoxytriphenylene was carried out by a trimerization of veratrole in the presence of sulfuric acid. Complexation of HMT and C_{60} fullerene was prepared by the treatment of 2,3,6,7,10,11-hexamethoxytriphenylene (2 equiv.) in chloroform or 1,1,2-trichloroethane solution with C_{60} molecules (1 equiv.) dissolved in toluene solution. The mixture was stirred at 80 °C for 30 min. and then maintained at that temperature for a period of 4h without stirring. During this heating period, the sharp octahedral purplish blue crystals were grown from the solution mixture. After cooling the solution to ambient temperature, the crystals were collected and washed repeatedly with chloroform and toluene to afford higher than 90% yield of complex. The elemental analysis of this complex is in good agreement with a chemical composition

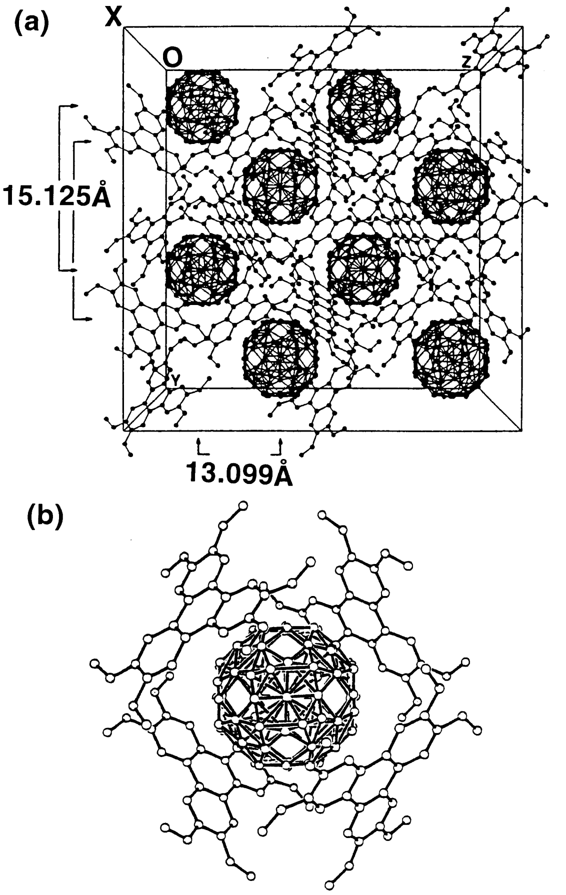


Fig. 1. (a) The molecular packing diagram for half of one $C_{60}(C_{24}H_{24}O_6)_2$ unit cell showing the dispersion of disordered C_{60} "atoms" inside the HMT matrix. Single crystals of **2** are, at 20±1 °C, cubic, space group $Fd3c$-O_h^8 (No. 228) with a = 30.251(9) Å, α = 90.00°, V = 27682(30) $Å^3$, Z = 16 (d_{calcd} = 1.476 gcm^{-3}; linear absorption coefficient μ_α(Cu K_α) = 0.77 mm^{-1}), and R_u (unweighted) = 0.098. (b) a partial molecular packing diagram of $C_{60}(HMT)_2$ complex showing a clear view of each C_{60} fullerene molecule surrounded by four HMT molecules in tetrahedral arrangement.

of $C_{60}(HMT)_2$ (**2**).10) Variation of HMT vs C_{60} ratio from 1 to 4 in the complexation reaction did not lead to complexes with a different chemical composition than that of **2**. The infrared spectrum of complex **2** showed most of the characteristic peaks of HMT, in close resemblance to those of pure HMT, and bands at 578 and 528 cm^{-1}, which correspond to the C_{60} moiety of the complex. The much stronger intensity of HMT vibrational absorptions than that of C_{60} peaks indicated a higher HMT content in the complex. There are slight deviations of absorption bands at about 1450 cm^{-1} and 1200 cm^{-1} regions compared to those of HMT. The most pronounced shift of peaks occurred at the absorption band of 864 cm^{-1}, which presents a shift of 21-31 wavenumber from a group of peaks at 843 and 833 cm^{-1} in the infrared spectrum of HMT. The nature of these shifts is not all clear. The spectrum was compared with that of the monocationic HMT, either in the electrochemically grown HMT^+-ClO_4^- salt11) or in the HMT^+-tris(dicyanomethylene)-cyclopropane ($HCTMC^-$) complex,12) showing a corresponding absorption band at 835 cm^{-1} or 843 cm^{-1}, respectively. The UV-visible spectrum of complex **2** in 1,1,2-trichloroethane displayed three absorption bands at 259, 268, and 278 nm and a shoulder peak centered at 310 nm with similar peak positions to those of HMT in the same solvent, but a different relative intensity among peaks, and a weak peak centered at 330 nm contributed from the C_{60} moiety. These spectroscopic data are consistent with the chemical structure of complex **2** as $C_{60}(HMT)_2$.

The unique structure of $C_{60}(HMT)_2$ was partially revealed first by the high resolution powder x-ray diffraction performed at the National Synchrotron Light Source. The ability to grow a large single crystal allowed single crystal x-ray crystallography to be carried for the complete structural analysis.13) Both results indicates that each cubic unit cell of **2** contains 32 ordered HMT donor and 16 partially rotationally disordered C_{60} acceptor moieties. Each HMT molecule possesses rigorous crystallographic D_3-32 symmetry in the crystal with unexceptional average C-C and C-O bond lengths of 1.40(2) Å and 1.41(2) Å, respectively; the C-C-C, C-C-O and C-O-C angles all averaged 120(1)°. These ordered HMT moieties determine a matrix of donor molecules with about 10 Å diameter spherical cavities around the tetrahedral T-23 sites which are occupied by the partially disordered C_{60} molecules (Fig. 1a). Each C_{60} molecule is surrounded in the lattice by four HMT donor molecules in a rigorous tetrahedral arrangement with a C_{60} to HMT center-of-gravity separation of 6.550 Å; if the radius of a C_{60} "sphere" is taken to be 3.55 Å,[14,15)] this corresponds to a 3.00 Å van der Waal's separation between the surface of the C_{60} sphere and the HMT center-of-gravity. A partial molecular packing diagram of the $C_{60}(HMT)_2$ complex showing a clear view of an encompassed C_{60} molecule is presented in Figure 1b. The shortest C_{60}-C_{60} center-of-gravity separation is 13.099 Å, in close resemblance to that of C_{60}-hydroquinone-C_{60} sandwich,[4)] and is between two C_{60} moieties along the body diagonal of the unit cell. The shortest HMT-HMT center-of-gravity separation of 10.695 Å is between HMT moieties related by a translation parallel to the diagonal of a unit cell face. The next shortest C_{60}-C_{60} and HMT-HMT center-of-gravity separations are both 15.125 Å and are between pairs of acceptors or donors which are separated by half of a unit cell edge.

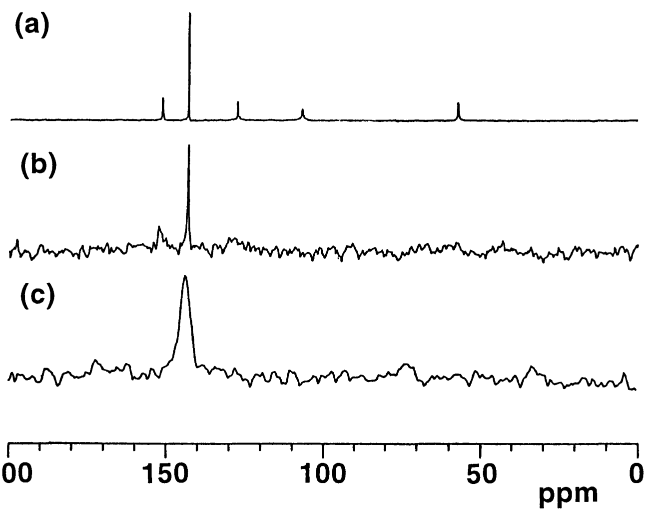


Fig. 2. ^{13}C solid state NMR spectra of $C_{60}(HMT)_2$ complex as (a) "normal" CP/MAS spectrum acquired with the proton decoupling, (b) CP/MAS spectrum acquired without the proton decoupling, and (c) "static" CP spectrum taken without the magic angle spinning. Spectra a, b, and c were all taken with a 3-second recycle delay and were the result of 560, 32, and 64 scans, respectively.

The ^{13}C solid state NMR normal CP/MAS (cross polarization/magic angle spinning) spectra of $C_{60}(HMT)_2$ complex, acquired with proton decoupling on a commercial 4.7 Tesla system, at either ambient temperature or -90 °C displayed five lines due to C_{60} (141.8 ppm) and HMT (150.0, 126.2, 106.1, and 56.0 ppm) as shown in Figure 2a. The chemical shift of carbons in the fullerene of complex is only slightly perturbed from that observed in the pure C_{60}. The resonances of carbons in HMT molecules show significant low-field shifts relative to those obtained in pure HMT,[16)] indicating a partial degree of electron transfer from HMT to C_{60}. In the CP/MAS experiment without utilizing the proton decoupling, the spectrum (Fig. 2b) gave a slight broadening of the C_{60} carbon peak at 141.8 ppm and the near disappearance of all HMT carbon peaks as expected. Finally, the "static" cross polarization experiment taken with the proton decoupling but without the use of magic angle spinning gave a single line centered at 143 ppm with a linewidth of about 5 ppm, considerably broader than the 0.1 ppm observed in the CP/MAS spectra (Fig. 2c), indicating incomplete averaging of the chemical shift anisotropy of the C_{60} carbons by their rapid tumbling motion in the solid state. The linewidth observed here is only slightly larger than the value of 2.5 ppm reported for pure C_{60},[17)] indicating that the presence of HMT molecules appears to have little effect on the motion of the C_{60} at least at ambient temperature. In conclusion, we have successfully synthesized the charge-transfer complex of C_{60}

fullerene with a symmetrical donor of 2,3,6,7,10,11-hexamethoxytriphenylene. All spectroscopic data and analyses support the chemical composition of this complex as $C_{60}(HMT)_2$. The complex crystallized in a cubic unit cell structure with dimensions larger than those found in the crystal of superconducting K_3C_{60}.14) Since it has not been possible to complex C_{60} fullerene with triphenylene, perylene, or some fulvalene-type electronic donors such as TTF and TMTSF (except BEDT-TTF5)) used in the study of organic electronic conductivity and superconductivity, the facile complexation of C_{60} with the relatively poor donor HMT (with the first half-wave oxidation potential of 0.92 V vs SCE in acetonitrile) will be of interest theoretically.

This work was supported by National Science Council of Republic of China (grant no. 82-0208-M-002-130).

References

1) Q. Xie, E. P. Cordero, and L. Echegoyen, *J. Am. Chem. Soc.*, **114**, 3978 (1992) and references therein.
2) P. M. Allemand, K. C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner, and J. D. Thompson, *Science*, **253**, 301 (1991).
3) A. Penicaud, J. Hsu, C. A. Reed, A. Koch, K. C. Khemani, P. M. Allemand, and F. Wudl, *J. Am. Chem. Soc.*, **113**, 6698 (1991).
4) O. Ermer, *Helv. Chim. Acta* , **74**, 1339 (1991).
5) A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito, and H. Shinohara, *J. Chem. Soc., Chem. Commun.*, **1992**, 1472.
6) R. Breslow, *Pure & Appl. Chem.*, **54**, 927 (1982); T. J. LePage and R. Breslow, *J. Am. Chem. Soc.*, **109**, 6412 (1987).
7) L. Y. Chiang, D. C. Johnston, D. P. Goshorn, and A. N. Bloch, *J. Am. Chem. Soc.*, **111**, 1925 (1989); L. Y. Chiang, R. B. Upasani, D. P. Goshorn, and J. W. Swirczewski, *Chem. Mater.*, **4**, 394 (1992).
8) J. S. Miller, D. A. Dixon, J. C. Calabrese, C. Vazquez, P. J. Krusic, M. D. Ward, E. Wasserman, and R. L. Harlow, *J. Am. Chem. Soc.*, **112**, 381 (1990).
9) L. Y. Chiang, H. Thomann, *J. Chem. Soc., Chem. Commun.*, **1989**, 172.
10) Elemental analysis of complex **2**: Found: C, 84.34; H, 3.18; O, 11.5%. Calcd C, 84.38; H, 3.13; O, 12.5%.
11) L. Y. Chiang, D. C. Johnston, J. P. Stokes, and A. N. Bloch, *Synth. Met.*, **19**, 697 (1987).
12) L. Y. Chiang, R. B. Upasani, D. P. Goshorn and J. W. Swirczewski, *Chem. Mater.*, **4**, 394 (1992).
13) A total of 672 independent reflections having $2\theta\,(CuK_\alpha) < 105.1°$ (the equivalent of 0.50 limiting CuK_α spheres) were collected. The resulting structural parameters have been refined to convergence [R_u (unweighted, based on F) = 0.098 for 397 independent reflections having $2\theta\,(CuK_\alpha) < 105.1°$ and $I > 3\sigma(I)$].
14) P. W. Stephens, L. Mihaly, P. L. Lee, R. L. Whetten, S. M. Huang, R. Kaner, F. Deiderich, and K. Holczer, *Nature*, **351**, 632 (1991).
15) K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo, and S. Kuroshima, *Nature*, **352**, 222 (1991).
16) ^{13}C solid state CP/MAS NMR spectrum of HMT: δ 52.9, 55.4, 102.4, 103.0, 122.0, 122.9, and 149.6.
17) R. Tycko, G. Dabbaugh, R. M. Fleming, R. C. Haddon, A. V. Makhija, and S. M. Zahurak, *Phys. Rev. Lett.*, **67**, 1886 (1991).

(Received January 31, 1994)