
ELECTRONIC PROPERTIES OF NOVEL MATERIALS— SCIENCE AND TECHNOLOGY OF MOLECULAR NANOSTRUCTURES

XIII International Winterschool

Kirchberg, Tirol, Austria February- March 1999

EDITORS

Hans Kuzmany

Universität Wien, Austria

Jörg Fink

Institut für Festkörper- und Werkstoff-Forschung

Dresden, Germany

Michael Mehring

Universität Stuttgart, Germany

Siegmar Roth

Max-Planck-Institut für Festkörperforschung

Stuttgart, Germany

AIP

American Institute of Physics

**AIP CONFERENCE
PROCEEDINGS 486**

Melville, New York

New Three-component Systems Based on C_{60}

Rimma N. Lyubovskaya*, Dmitry V. Konarev, Evgeniya I. Yudanova,
Yury M. Shul'ga, Natalia V. Drichko¹, Yan V. Zubavichus².

Institute of Problems of Chemical Physics RAS, 142 432 Chernogolovka, Russia.

¹*A. F. Ioffe Physical-Technical Institute RAS, 194021, St. Petersburg, Russia.*

²*Institute of Organoelement Compounds RAS, 117334, Vavilov St. 28, Moscow, Russia*

Abstract. For the first time the C_{60} complex, $C_{60}(\text{BEDT-TTF}^+)(\text{I}_3^-)$, comprising the radical cation of the organic donor BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) was synthesized. Single crystals of the complex were obtained in benzonitrile. This compound has C-centered monoclinic lattice with the unit cell parameters: $a=17.419(6)$, $b=9.997(4)$, $c=13.499(1)$ Å, $\beta=99.00(1)^\circ$. The bands characteristic of the BEDT-TTF^+ cation radical and neutral C_{60} are present in IR- and optical reflectivity spectra of single crystals and optical absorption spectra in KBr pellets. The signal with $g=2.0074$ and $\Delta H_{pp}=23\text{G}$ is attributed to BEDT-TTF^+ in the EPR spectrum. The position of $13d_{5/2}$ peak confirms the formation of the I_3^- anion.

INTRODUCTION

Tetrathiafulvalene derivatives are known to be widely used in the design of radical cation salts which manifest metallic and superconducting properties. For example, a family of BEDT-TTF based superconducting radical cation salts, namely, $(\text{BEDT-TTF})_2\text{X}$, $\text{X}=\text{I}_3^-$, IBr_2^- , AuI_2^- , ReO_4^- , $\text{Cu}(\text{NCS})_2^-$ and $(\text{BEDT-TTF})_4\text{Hg}_{2.89}\text{Hal}_8$, $\text{Hal} = \text{Cl}$, Br has been synthesized¹.

However fullerene C_{60} forms only neutral complexes with tetrathiafulvalene derivatives, namely, with bis(ethylenedithio)tetrathiafulvalene $(\text{BEDT-TTF})^2$, dibenzotetrathiafulvalene³, octamethylenetetrathiafulvalene⁴ and others⁵⁻⁶.

To change a neutral state of molecular complexes of C_{60} , we intercalated the $\text{D}_k\text{C}_{60}(\text{Solv})_x$ (D is donor, Solv is a solvent) compounds by iodine in gas phase. During intercalation the solvent is substituted by iodine and the donor is oxidized in solid state to a radical cation or a dication to form a three-component system $\text{D}_k^+\text{C}_{60}\text{I}_n^-$, $n>5$ ⁷. However, gas-phase intercalation is a diffusion process and homogeneity of the resulting samples is hardly attained.

The present paper reports on the synthesis of the first three-component complex of C_{60} in solution which contains the (BEDT-TTF^+) radical cation, namely, $C_{60}(\text{BEDT-TTF}^+)(\text{I}_3^-)$. The crystal lattice parameters are determined. IR absorption spectra and polarized electron reflectivity spectra are measured on single crystals. The data on EPR and X-ray photoelectron spectra are presented.

EXPERIMENTAL

BEDT-TTF- $I_{3,4}$, $x \sim 3.4$ was used as a starting compound in the synthesis of $C_{60}(\text{BEDT-TTF-}I_3)$. $C_{60}(\text{BEDT-TTF-}I_3)$ was prepared by cocrystallization of stoichiometric quantities of BEDT-TTF- $I_{3,4}$ and C_{60} in benzonitrile. The compound was prepared as rhomb-like crystals up to 0.5 mm in size. Found, %: C 56.4; H 0.74; S 17.14; I 26.20. $S_8C_{70}H_8I_3$. Calculated, %: C 56.7; H 0.53; S 17.14; I 25.6.

The IR transmission spectrum of the $C_{60}(\text{BEDT-TTF-}I_3)$ single crystals was measured within the 650–4000 cm^{-1} range on the Perkin-Elmer 1760 IR spectrometer equipped with a microscope. Electron reflectivity spectra of single crystals were measured on a home made double-beam microspectroreflectometer. X-ray photoelectron spectra were excited by Mg-K α -radiation ($h\nu=1253.6$ eV). The spectra were calibrated as to the peak C1s (285.0 eV). The data of X-ray powder diffraction were obtained on the DRON-3 automatic diffractometer with Cu-K α radiation ($\lambda=1.5418$ Å) and graphite monochromator.

RESULTS AND DISCUSSION

Compound $C_{60}(\text{BEDT-TTF-}I_3)$ has the following parameters of monoclinic crystal face-centered unit cell: $a=17.419(6)$, $b=9.997(4)$, $c=13.499(1)$ Å, $\beta=99.00$ (1°), $V=2321.8$ Å³. All the observed reflections were indexed and no systematic exclusions

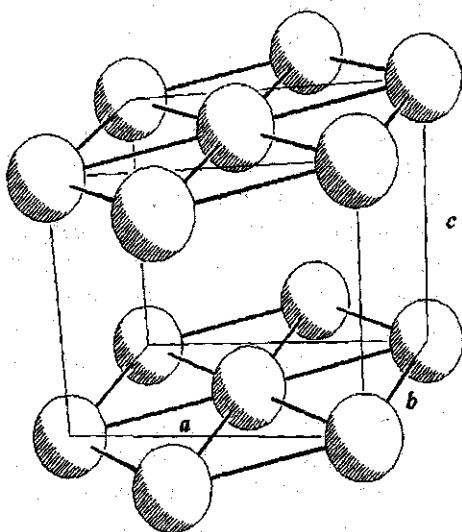


FIGURE 1. The diagram of the position of C_{60} molecules in the crystal lattice of $C_{60}(\text{BEDT-TTF-}I_3)$. C_{60} molecules are marked by spheres, crystallographic directions and the shortest distances between the centers of C_{60} molecules are marked by thin lines.

from the monoclinic face-centered lattice were observed. Therefore, the space groups $C2$, Cm or $C2/m$ are possible for the unit cell. Every fullerene molecule can be surrounded by six almost equidistant neighbouring C_{60} molecules. In this case two fullerene molecules with the 10.00 Å distances between the centers (translation vectors are $0 \pm 1 \ 0$) and the four neighbouring C_{60} molecules with the 10.04 Å distances between the centers (translation vectors are $\pm 0.5 \pm 0.5 \ 0$) can be located in the ab plane (see Fig.1). Therefore, one can assume that fullerene molecules form slightly distorted close-packed layers parallel to the

ab plane. The distances between these layers are 13.5 Å. The BEDT-TTF⁺ radical cations and the I₃⁻ anions can occupy cavities in the interlayer space. Such layered structures are characteristic of C₆₀ complexes with substituted tetrathiafulvalenes, in which donor and solvent molecules are located between close-packed fullerene layers^{4,6}.

The IR transmission spectrum of the C₆₀(BEDT-TTF·I₃) single crystals represents the absorption bands at 1429 and 1182 cm⁻¹ characteristic of C₆₀. Their position remains unchanged as compared with that in the spectrum of initial C₆₀, indicating the absence of noticeable charge transfer to the fullerene molecule. The spectrum also demonstrates the absorption bands characteristic of the BEDT-TTF⁺ radical cation: 1384, 1289, 1021, 927, 899, 882, and 808 cm⁻¹. Their positions are close to those of absorption bands observed earlier for the BEDT-TTF⁺ radical cation in the transmission spectrum of the BEDT-TTF·I₃ radical cation salt⁸.

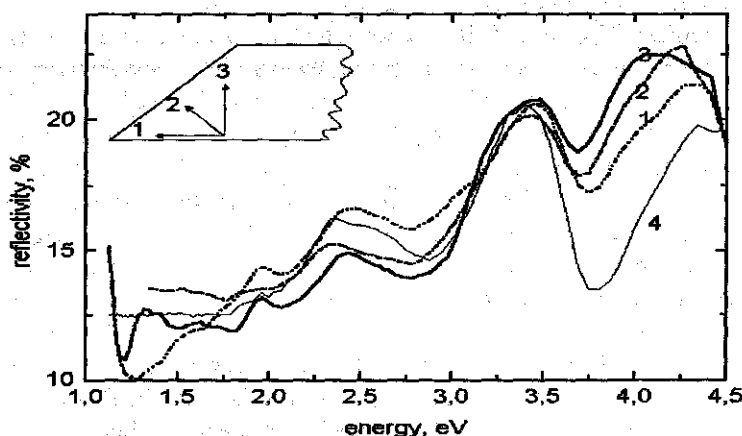


FIGURE 2. Electronic reflectivity spectra of the C₆₀(BEDT-TTF·I₃) single crystals measured from the developed plane for three polarizations (1, 2, 3) and the reflectivity spectrum of the initial C₆₀ crystal (4).

Electron polarized reflectivity spectra of the C₆₀(BEDT-TTF·I₃) single crystals were measured from the larger crystal face for three polarizations (see Fig.2). This spectrum exhibits the peaks at 4.2, 3.6, 2.5, and 1.1 eV and a relatively weak peak at 1.96 eV. The positions of peaks of C₆₀ at 4.2 and 3.6 eV in the complex are close to those of pure C₆₀, however the peaks are essentially broadened. Such a broadening was observed earlier at intercalation of fullerene complexes by iodine⁷. The reflectivity band at 2.5 eV can be attributed mainly to intermolecular charge transfer between HOMO-LUMO of the neighbouring C₆₀ molecules⁹. This band has approximately equal intensity in the spectrum of C₆₀(BEDT-TTF·I₃) and the crystals of pure C₆₀.

A reflectivity band at 1.1 eV can be attributed to BEDT-TTF⁺. This band is weakly polarized, the highest intensity is observed in the polarization «1». The similar band was observed in polarized spectra of the (BEDT-TTF)₂I₃ single crystals¹⁰.

Table 1. Binding energies (E_b) and half-widths (Δ) of XP lines. All the values are in eV and calibrated as to the peak C1s (285.0 eV).

Compound	Δ C1s	S2p	Δ S2p	I3d _{5/2}	Δ I3d _{5/2}
C ₆₀ (BEDT-TTF·I ₃)	2.1	164.1	2.6	619.4	2.3
(BEDT-TTF) ₂ I ₃ ¹¹	2.0	163.8	2.4	619.0	2.1
BEDT-TTF	1.9	163.6	2.4	-	-
(Ph ₄ P) ₂ C ₆₀ ·I ¹²	2.1	-	-	617.7	2.2

Table 1 shows half-widths and positions of the peaks C1s, S2p, and I3d_{5/2} in XP spectra of C₆₀(BEDT-TTF·I₃).

A positive shift of the S2p binding energy is observed at changing from BEDT-TTF to C₆₀(BEDT-

TTF·I₃). This corresponds to the decrease of electron density on sulfur atoms at changing from neutral BEDT-TTF to the radical cation state in C₆₀(BEDT-TTF·I₃).

The position of the peak I3d_{5/2} with E_b =619.4 eV in this compound is close to its position in (BEDT-TTF)₂I₃¹¹. This indicates that the sample under study contains iodine as the I₃⁻ anion since for I⁻ anion essentially lower binding energy is characteristic, for example, in (Ph₄P)₂C₆₀(I⁻) E_b is equal to 617.7 eV¹².

EPR studies of the spectra of C₆₀(BEDT-TTF·I₃) at room temperature showed the presence of an intense EPR signal with g =2.0074 and ΔH_{pp} =23 G corresponding to the BEDT-TTF⁺ radical cation. With the temperature decrease the position of g -factor and the width of the EPR signal remain almost unchanged and g =2.0074, ΔH_{pp} =20 G (77 K). Such a behaviour is different from that of (BEDT-TTF)₂I₃ which is characterized by a noticeable narrowing of the EPR signal with the temperature decrease¹. The integral intensity of the signal in C₆₀(BEDT-TTF·I₃) increases 2.2 times with the temperature decrease from 300 down to 77 K. Such a behaviour of the EPR signal is the most probably associated with electron localization over the BEDT-TTF⁺.

Conductivity of C₆₀(BEDT-TTF·I₃) measured on a pressed pellet amounts to 2·10⁻⁴ Ohm⁻¹cm⁻¹. This value is two orders of magnitude higher than conductivity of the (BEDT-TTF)₂C₆₀ complex (10⁻⁶ Ohm⁻¹cm⁻¹) measured under the same conditions. The low value of conductivity is assumed to be due to integer-valued charge on the BEDT-TTF molecule (+1) and is characteristic of other BEDT-TTF radical cation salts with full charge transfer¹.

ACKNOWLEDGEMENTS

This work is supported by the Russian program «Fullerenes and Atomic Clusters» and Russian Foundation for Basic Research, project N98-02-18303.

REFERENCES

1. Williams J.M., Ferraro J.R., Thorn R.J., Carlson K.D., Geiser U., Wang H.H., Kini A.M., and Whangbo M.-H., *Organic Superconductors (including Fullerenes). Synthesis, Structure, Properties and Theory*, Prentice Hall, Englewood Cliffs, New Jersey, 1992.
2. Izuoka A., Tachikawa T., Sugawara T., Suzuki Y., Konno M., Saito Y., Shinohara H., *J.Chem.Soc., Chem.Comm.*, 1472 (1992).
3. Konarev D.V., Zubavichus Y.V., Slovokhotov Yu.L., Shul'ga Yu. M., Semkin V.N., Drichko N.V., and Lyubovskaya R.N., *Synth.Met.*, **92**, 1 (1998)
4. Saito G., Teramoto T., Otsuka A., Sugita Y., Ban T., Kusunoki M., and Sakaguchi K.-I., *Synth. Met.*, **64**, 359 (1994).
5. Konarev D.V., Valeev E.F., Slovokhotov Yu.L., Shul'ga Yu.M., et.al. *Synth.Met.*, **88**, 85(1997)
6. Llacay J., Tarres J., Veciana J., Rovira C., Veciana J., Mas M., and Molins E., *J.Phys.Chem.Solids*, **58**, 1675 (1997)
7. Lyubovskaya R.N., Konarev D.V., and Yudanov E.I., et.al., *Synth. Met.*, **84**, 741 (1997).
8. Kozlov M.E., Pohodnia K.L., and Yurchenko N.M., *Spectrochimica Acta*, **45A**, 437 (1989).
9. Saeta P.N., Greene B.I., Kortan A.R., Kopylov N., and Thiel F.A., *Chem.Phys.Lett.*, **190**, 184 (1992).
10. Vlasova R.M., Prieв S.Ya., Semkin V.N., et.al., *Fizika Tverdogo Tela (in Russian)*, **32**, 448 (1990).
11. Konarev D.V., Lyubovskaya R.N., Shul'ga Yu.M., *Dokladii RAS (in Russian)*, **346**, 490 (1996).
12. Shul'ga Yu.M., Spitsyna N.G., and Yagubskii E.B., *Dokladii RAS (in Russian)*, **348**, 502 (1996)