Preparation and investigation of the crystals formed in the buckminsterfullerene—tetraselenotetracene—carbon disulfide system

E. E. Laukhina,[a] *Yu. M. Shul'ga,*[a]* *V. I. Rubtsov,*[a] *V. N. Vasilets,*[b] *V. P. Bubnov,*[a]
E. B. Yagubskii,[a] *N. V. Avramenko,*[c] *and M. N. Frolova*[c]

[a]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588
[b]*Branch of the Institute of Energetic Problems of Chemical Physics, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation
[c]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
119899 Vorob'evy Gory, Moscow, Russian Federation.
Fax: +7 (095) 939 5546

Crystals containing up to 30 wt. % CS_2, according to the data of IR and X-ray photoelectron spectroscopy, were isolated from the C_{60}—TSeT—CS_2 (TSeT is tetraselenotetracene) system. The unusually high concentration of carbon disulfide results in the complete sublimation of the crystals at a relatively high temperature (520 °C). The electron energy loss spectra of the crystals obtained were measured and analyzed.

Key words: fullerenes; XP spectra; IR spectra; EEL spectra; differential thermal analysis.

The synthesis of a complex between buckminsterfullerene (C_{60}) and tetrathiotetracene (TTT) has previously been reported.[1,2] It seemed of interest to obtain a compound of C_{60} with another planar molecule (an organic donor), tetraselenotetracene (TSeT), which has the same structure as TTT and similar physicochemical properties. Since the solubilities of TSeT and C_{60} in benzene and toluene differ, the attempts to obtain a complex by the method of cocrystallization with a programmed increase in the temperature of the mother liquor failed: first TSeT crystals grew and then a precipitate containing mainly C_{60} formed. The use of CS_2, a solvent in which the solubilities of the both components are approximately the same, allowed us to grow large needle-like crystals (20×2×1 mm). The analysis shows that they contain a large amount of CS_2 (up to 30 wt. %) and the fraction of TSeT is too small to consider the crystals obtained as a compound of C_{60} and TSeT.

It is known that the concentration of a solvent can be high in clathrates of C_{60} with the solvent. The crystals of C_{60} isolated from CS_2 are also needle-like and contain from 0.2 to 3.6 wt. % CS_2 (see Ref. 3). Crystals based on C_{60} with a higher concentration of CS_2 (up to 30 wt. %) and stable in air have not been described in the literature. In this connection, here we present the results of the studies of the crystals obtained by X-ray photoelectron spectroscopy (XPS), IR spectroscopy, differential thermal analysis, and electron energy loss spectroscopy (EELS).

Experimental

A solution (40 mL) containing 36 mg of C_{60} and 18 mg of TSeT in CS_2 was placed in a 100-mL glass crystallizer. After 6 to 7 days of slow evaporation of carbon disulfide, long (>10 mm) black shiny needles were formed on the bottom of the crystallizer and a fine crystalline precipitate was formed on the walls of the crystallizer. The needle-like crystals were carefully washed off with dehydrated EtOH and dried in air. A crystalline substance (crystals **LL1**, 10 mg) was obtained.

IR spectra were recorded on a Perkin Elmer 1720X IR-Fourier spectrometer (0.5 cm^{-1} resolution), using a diffuse reflectance attachment (Perkin Elmer, angle of incidence 38°, angle of scattered light collection 180°). Samples were prepared by mixing the compound studied with KBr powder. When the concentration of the substance studied was ≤3 wt. % in the mixture, the diffuse reflectance (DF) spectrum coincided with the absorption spectrum of the sample.[4] The IR absorption spectra for pellets of fullerene with KBr and the IR DF spectrum of C_{60} presented in the literature[5—7] also agree with those obtained in this work. Unlike the traditional procedure of the preparation of pellets with KBr, the procedure of diffuse reflectance is not distorting, because it does not require molding, it is more sensitive (the signal/noise ratio is proportional to $C^{0.5}$, where C is the concentration of a substance), and it balances out the lines of water and other admixtures in KBr almost completely. However, to estimate the composition, IR transmission spectra of pellets of a mixture of **LL1** crystals and reference compounds (C_{60} and TSeT) with KBr were also recorded with 4 cm^{-1} resolution.

Samples for studying the induced electron emission spectra were prepared by depositing a thin layer of a powder of a

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 845—848, May, 1995.

compound to be studied on an aluminum holder whose surface had been preliminarily cleaned, and then oxidizing them in air to form a thin (40 Å) layer of Al_2O_3. The existence of such a layer excludes the possible interaction of the compound studied with metallic Al, and at the same time, does not prevent the electrical contact between the sample with the substrate.

Electron spectra were recorded on a PHI-551 instrument equipped with a double cylindric mirror type analyzer. Mg-Kα-irradiation ($h\nu$ = 1253.6 eV) was used for the excitation of XP spectra. The analyzer worked in the retardation potential mode (the energy of electrons passing through the analyzer (E_0) was 50 eV) at an absolute resolution of 1.1 eV. EEL spectra were excited by the electron beam from an electron gun coaxial with the analyzer. The energy of the primary electron beam was equal to 2 keV. The half-width of the energy distribution for the primary beam was 0.5 eV. EEL spectra were recorded in the retardation potential mode: E_0 = 25 eV, absolute resolution was 0.6 eV. The pressure of residual gases in the chamber of the spectrometer during the measurements did not exceed $3 \cdot 10^{-10}$ Torr.

The transition from the integral intensities measured in the XP spectra to atomic concentrations was performed using Skofield's data on the photoelectron absorption cross-sections of the Mg-Kα-irradiation.[8]

The measured spectra were adjusted, taking into account the dependence of the transmission coefficient of the analyzer on the kinetic energy. Single loss spectra, $y(E)$, were determined from the solution of the integral equation[9]

$$N^{\mathrm{in}}(E) - ky(E)*N^{\mathrm{in}}(E) = ky(E),$$

where the sign * designates the energy convolution; $N^{\mathrm{in}}(E)$ is the inelastic part of the EEL spectrum measured normal to the surface area under the elastic peak; k is a factor that takes into account the geometry of the electron reflectance experiment.

The function $y(E)$ thus obtained is proportional to the loss function averaged over the scattering angles[9]

$$y(E) \sim \ln(1 + \theta_{\max}{}^2/\theta_E{}^2)Im(1/\varepsilon(E)),$$

where $\theta_{\max}$ is the maximum angle of scattering on the electrons of the valence shell, $\theta_E = E/(2E_{\mathrm{pr}})$ (E_{pr} is the energy of the primary beam). One of the advantages of this approach is that it does not require special assumptions about the particular energy dependence of the differential cross-section of inelastic scattering for plasmon and other channels of electron scattering. The sequence of procedures for the isolation of the function $y(E)$ from the experimental spectrum of C_{60} is given in the literature.[10]

The thermal stability of crystals was studied on a DSC-30 differential scanning calorimeter (Mettler). Reference substances (hexane, water, gallium, indium, *p*-nitrotoluene, lead, and zinc) were used for the temperature calibration of the calorimeter. The experiments were carried out in aluminum crucibles in a nitrogen atmosphere; the scanning rate was 20 K min^{-1}. The weight of a sample was 8.127±0.002 mg. Samples were heated in the 108 to 293 K temperature range. The differential thermal analysis was performed on a Mettler thermobalance in a nitrogen atmosphere at 298 to 973 K with a heating rate of 20 K min^{-1}.

Results and Discussion

The IR spectra of the compound studied are presented in Fig. 1.

The positions of the most intense absorption bands (AB) in the spectrum of the compound studied almost coincide with the frequencies of the most intense AB in

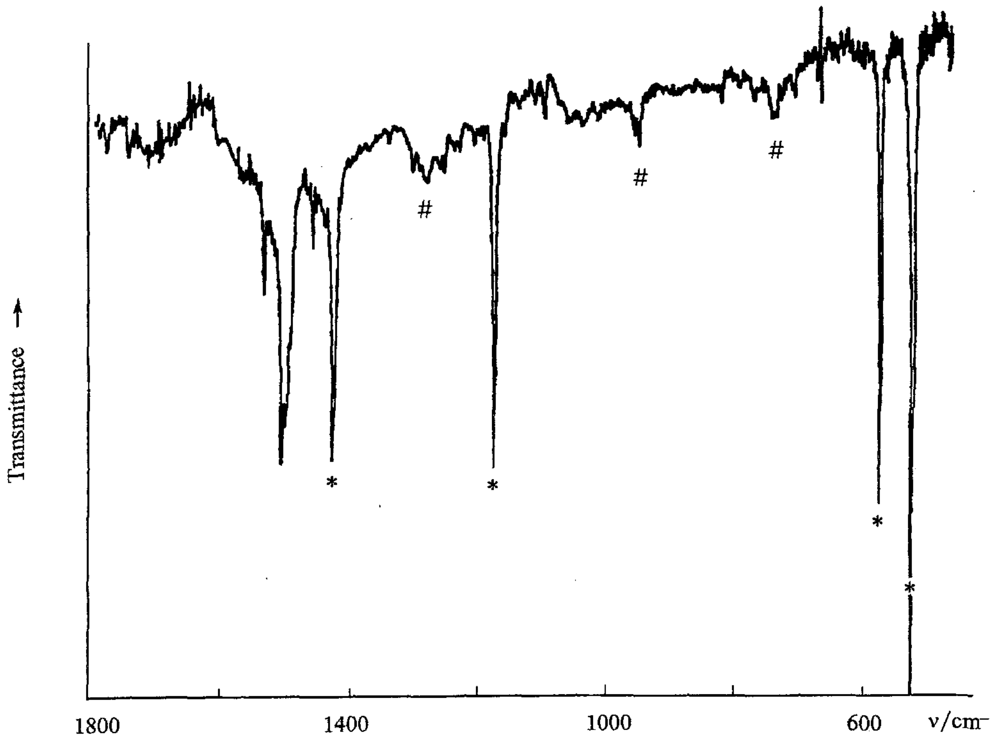

Fig. 1. IR spectrum of the crystals studied. The most intense absorption lines of C_{60} and TSeT are denoted by the signs * and #, respectively.

the spectrum of C_{60} (Table 1), which allows us to assign these AB to the vibrations of buckminsterfullerene atoms. The spectra of the crystals studied differ from those of fullerite by the 1 cm^{-1} shift of the AB at 576 cm^{-1}.

The relative intensities of the AB are also an interesting parameter. It has previously been established[11] that the intensities of all AB increase on going from C_{60} to A_xC_{60} (where A is an alkaline metal atom). However, the integral intensity of the AB at 526 cm^{-1} varies only twofold at $x = 6$. It is reasonable to assume that the change in intensity of the AB at 526 cm^{-1} can be neglected for a small charge transfer ($x < 1$), *i.e.*, this band can be used as an internal standard for measuring the integral intensities of the other AB related to the vibrations of the atoms of C_{60}. It is also noteworthy that the assumption about a small charge transfer in the compound studied agrees with the insignificant shifts of the main AB. It can be seen from the data in Table 1 that the intensities of all AB increase, and the intensity of the AB at 1183 cm^{-1} increases nearly fourfold. These changes can be related to the distortion of the symmetry of the nearest surroundings of the fullerene molecules.

The positions of the three weak AB in the spectrum of the compound studied (1284.5, 955.5, and 746.0 cm^{-1}) marked by the sign # in Fig. 1 coincide with those of the most intense bands of TSeT or are close to them (1285, 955.5, and 740.5 cm^{-1}). The estimation of the content of TSeT performed with the assumption that the extinction coefficients of these AB in the crystals studied are the same as those in TSeT shows that there are no more than 5 TSeT molecules per 100 molecules of C_{60}.

Finally, the AB at 1509.5 cm^{-1} and the shoulder at 1503.5 cm^{-1} in the spectrum of the compound studied are caused by the stretching vibrations of CS_2 (see Ref. 12). It is rather difficult to estimate with sufficient reliability the fraction of this component from the IR spectra. The differential method gives ~30 wt. %.

The composition of the crystals studied was estimated quantitatively from the changes in the integral intensities of the C 1s, S 2p, and Se 3d peaks in the XP spectra (Table 2). The $[Se/Cl]_{at}^{XPS}$ ratio was equal to 0.003, which corresponds to 4.5 TSeT molecules per 100 molecules of C_{60} and virtually coincides with the data of IR spectroscopy. The $[S/C]_{at}^{XPS}$ ratio (0.047) corresponds to ~1.4 CS_2 molecules per 1 molecule of C_{60}, which is considerably lower than the value estimated from the IR spectra (4 molecules of CS_2 per 1 molecule of C_{60}). However, the $[S/Cl]_{at}^{XPS}$ ratio also cannot be considered exact, because the surface layer of the compound studied can be depleted in sulfur due to the partial desorption of CS_2 in a high vacuum under irradiation with X-ray quanta. A similar effect has previously[13] been observed in studying the composition of the surface of $C_{60} \cdot 2S_8$. Taking this into account, it should be considered that there are 1.5 to 4 molecules of CS_2 per 1 molecule of C_{60} in the crystals studied. It is noteworthy that the sample of $C_{60}(CS_2)_x$, which was obtained under the same conditions as the crystals studied, but without addition of TSeT to the mother liquor, contains more than an order of magnitude less sulfur than the **LL1** crystals in the zone analyzed by XPS.

Thus, the volume composition of **LL1** samples testifies in favor of a small admixture of TSeT in these crystals. However, the role of such an admixture is extremely important: the samples synthesized without TSeT contain no more than 0.1 molecules of CS_2 per 1 molecule of C_{60}. According to the literature data,[3] the admixture of sulfur in orthorhombic crystals of C_{60} isolated from a solution of CS_2 ranges within 0.6 to 3.6 at. %, which corresponds to 0.2 to 1.0 molecules of CS_2 per 1 molecule of C_{60}.

The positions of the maxima of the individual peaks in the XP spectra of the **LL1** crystals and the compounds taken for comparison are also presented in Table 2. It can be seen that the Se 3d line in the spectrum of the crystals studied is shifted 0.8 eV toward lower bond energies relative to the spectrum of pure TSeT. The relatively small half-width of the C 1s peak in the XP spectrum of **LL1** is another specific feature. The high degree of homogeneity of the crystals studied may be one of the reasons for this peculiarity.

The form of the loss function of the **LL1** crystals resembles that of pure fullerite. However, the energy of the ($\sigma + \pi$)-plasmon for the **LL1** crystals is approximate-

Table 1. Positions (ν_x) and relative integral intensities ($I^0(\nu_x) = I(\nu_x)/I(\nu_1)$) of the main AB caused by the vibrations of the atoms of C_{60} in pure fullerite and crystals **LL1**

Parameter	Sample	
	LL1	C_{60}
ν_1/cm^{-1}	527.0	527.0
ν_2/cm^{-1}	577.0	576.0
ν_3/cm^{-1}	1183.0	1183.0
ν_4/cm^{-1}	1429.5	1429.5
$I^0(\nu_2)$	0.49	0.48
$I^0(\nu_3)$	2.00	0.56
$I^0(\nu_4)$	1.69	0.93

Table 2. Positions (E_b) and half-widths (Δ) of the lines of the XP spectra and the concentrations of the elements determined from the integral intensities of the XPS lines, using photoionization cross-sections[8]

Sample	E_b/eV			[C]*	[S]*	[Se]*
	ΔC 1s	Se 3d	S 2p			
C_{60}	1.3	—	—	100	—	—
$C_{60}(CS_2)_x$**	1.6	—	—	99.8	0.2	—
LL1	1.3	55.9	164.1	95.4	4.3	0.3
TSeT	1.6	56.7	—	78.5	—	21.5
S_8	—	—	163.8	—	100	—

* In at. %. ** The sample is obtained under the same conditions as crystals **LL1**.

ly 1.5 eV lower than the similar value for C_{60}. It is likely that the density of valence electrons in the crystals studied is lower than in fullerite. The relative intensity of the peak caused by the losses to excite the π-plasmon in **LL1** is higher than in C_{60}. It is probable that the increase in the intensity of the peak related to π-plasmon is caused by the high concentration of carbon disulfide in the crystals studied, because the fraction of π-electrons in CS_2 is higher than that in C_{60}.

The pronounced endothermic peak in the region from 203 to 240 K in the DSC curves of the **LL1** crystals attests unambiguously to a first-order phase transition. The temperature of the maximum of the peak is 228.1 K, and the heat of the transition is 1.6 J g^{-1}. It should be mentioned that such a low value is characteristic of "loose" systems. It is evident that the transition is related to the orientation ordering of C_{60} molecules in the crystals studied. Similar ordering has previously been observed for fullerite C_{60} at 250 K. The orientation disordering in crystals of **LL1** makes their crystallographic analysis difficult. Superficially well formed crystals give blurred relectances in the diffraction patterns obtained at room temperature, which does not allow one to resolve their structure.

The thermal stability of the **LL1** crystals was also studied in the range from 298 to 973 K by differential thermal analysis. Two temperature intervals where the sample loses its mass are observed on the TA and DTA curves. The first of them (440 to 534 K, Δm = 26 %) corresponds to the complete removal of CS_2 from the sample, and the second interval (738 to 919 K, Δm = 74 %) corresponds to the sublimation of C_{60}. It should be mentioned that the mass loss in the first temperature interval is stepwise: the first peak in the DTA curve at 455 K corresponds to the mass loss Δm = 7.49 %, while the second peak at 509 K corresponds to a 19.52 % mass loss. It is likely that CS_2 molecules exist in the crystals in two different conformations or occupy two different crystallographic positions. In the IR spectrum of the crystals, the AB caused by the vibrations of CS_2 also has two peaks.

In our opinion, the complete sublimation of C_{60} at a relatively low temperature (peak at 519 °C) is of extreme significance. The sublimation of solid samples of buckminsterfullerene in a nitrogen atmosphere usually begins at 600 °C, and its maximum rate is achieved at 700 to 800 °C (see, for example, Ref. 14). This may occur due to the partial polymerization of C_{60}. The great number of CS_2 molecules in the crystals prevents the polymerization of buckminsterfullerene molecules. This specific feature of the crystals makes it possible to assume that they can be used for the preparation of intense molecular beams.

This work was financially supported by the Russian Foundation for Basic Research (Projects No. 93-03-18002, 93-03-18705, and 93-03-5650).

References

1. G. Saito, T. Teramoto, A. Otsuka, Y. Sugata, T. Ban, M. Kusunoki, and K. Sakaguchi, *J. Phys. Soc. Jpn.*, 1994, **64**.
2. N. G. Spitsina, V. N. Semkin, and A. Graja, *Sol. State Commun.*, 1994.
3. T. Arai, Y. Murakami, H. Suematsu, K. Kikuchi, Y. Achiba, and I. Ikemoto, *J. Phys. Soc. Jpn.*, 1992, **62**, 1821.
4. P. J. Brimmer, P. R. Griffiths, and N. J. Harrick, *Appl. Spectrosc.*, 1986, **40**, 258.
5. W. Kratschmer, K. Fostiropoulos, and D. R. Huffman, *Chem. Phys. Lett.*, 1990, **170**, 167.
6. D. S. Bethune, G. Meijer, W. C. Tang, H. J. Rosen, W. G. Golden, H. Seki, C. A. Brown, and M. S. de Vries, *Chem. Phys. Lett.*, 1991, **179**, 181.
7. N. D. Kushch, I. Majchrzak, W. Ciesielski, and A. Graja, *Chem. Phys. Lett.*, 1993, **215**, 137.
8. *Methods of Surface Analysis,* Ed. A. W. Czanderna, Elsevier, Amsterdam—Oxford, 1975.
9. G. M. Mikhailov and V. I. Rubtsov, *Poverkhnost'* [*Surface*], 1987, No. 7, 99 (in Russian).
10. V. I. Rubtsov and Yu. M. Shul'ga, *Zh. Eksp. Teor. Fiz.*, 1993, **103**, 2065 [*Sov. J. Exp. Theor. Phys.*, 1993, **103** (Engl. Transl.)].
11. K.-J. Fu, W. L. Karney, O. L. Chapman, S.-M. Huang, R. B. Kaner, F. Diederich, K. Holczer, and R. L. Whetter, *Phys. Rev. B*, 1992, **46**, 1937.
12. R. S. Drago, *Physical Methods in Chemistry*, W. B. Saunders Comp., Philadelphia, 1977.
13. Yu. M. Shul'ga, V. I. Rubtsov, V. N. Vasilets, A. S. Lobach, N. G. Spitsyna, and G. A. Volkov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 2149 [*Russ. Chem. Bull.*, 1994, **43**, 2030 (Engl. Transl.)].
14. J. A. Milliken, T. M. Keller, A. P. Baronavski, S. W. McElvany, J. H. Callahan, and H. H. Nelson, *Chemistry of Materials*, 1991, 386.

Received November 25, 1994