A complex of buckminsterfullerene with sulfur, $C_{60} \cdot 2S_8$: synthesis and crystal structure

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The $C_{60} \cdot 2S_8$ complex was prepared by reaction of buckminsterfullerene C_{60} with sulfur in trichloroethylene and its single-crystal X-ray structure was studied at room temperature. Crystals of this compound are monoclinic, space group $C\,2/c$, a = 20.90(1), b = 21.10(1), c = 10.537(9) Å, β = 111.29(7)°, Z = 4, d_{calc} = 1.89 g · cm^{-3}. The crystal structure of the $C_{60} \cdot 2S_8$ complex consists of packed fullerene molecules that form hexagonal channels along the c axis with eight-membered crown-shaped S_8 cyclic molecules inside the channels. The distances between the centers of neighboring fullerene molecules are 10.036(7), 10.636(7), and 10.537(9) Å. Each C_{60} molecule is linked to eight S_8 molecules with ten shortened intermolecular contacts C...S 3.41(1)—3.52(2) Å. The average values of the C=C and C—C bond lengths are 1.32(3) and 1.47(3) Å, which attest to a significant degree of localization of electron density in the C_{60} molecule.

Key words: $C_{60} \cdot 2S_8$; fullerene complexes; synthesis; crystal structure.

Buckminsterfullerene C_{60} is a weak acceptor that forms charge-transfer complexes,[1—5] or ion-radical salts (fullerides)[6—8] with electron-donors depending on their donor ability. Some fullerides possess superconductivity or ferromagnetism.[6—7] Spherical shape and high negative reduction potentials are characteristic of a C_{60} molecule as an acceptor.[9] The latter factor determines in particular the low stability of fullerides in air. However, charge-transfer complexes with C_{60} are stable, and some of them (with donors $C_6H_4(OH)_2$, twin BEDT-TTF, BEDT-TTF, $(C_5H_5)_2Fe$) are isolated as single crystals.[1—4] Analysis of the structures of these complexes shows that the nature of the donor considerably affects the packing and stability of the charge-transfer complexes with C_{60}. However, the criteria of donor selection for complexes based on C_{60} with charge transfer have not yet been clearly defined. Conformational flexibility is an important structural feature[2,3] of a donor molecule acting as a component of charge-transfer complexes with C_{60}. Donors able to change their conformation by adapting themselves to the rigid spherical shape of C_{60} seem to be preferred for the formation of stable charge-transfer complexes with buckminsterfullerene.

Here we report the synthesis and crystal structure of a C_{60} complex with elemental sulfur having the composition $C_{60} \cdot 2S_8$. The choice of sulfur as a donor component was determined not only by its ability to form charge-transfer complexes with organic compounds,[10] but also by the expected conformation flexibility of the cyclic crown-shaped S_8 molecule.[11] It is also known that sulfur forms solid solutions with fullerenes.[12]

Experimental

The $C_{60} \cdot 2S_8$ complex was prepared by the reaction of C_{60} (0.01 mol) with sulfur (0.15 mol) in trichloroethylene, which here is used as the solvent for C_{60} for the first time. In a study of extraction of fullerenes from soot obtained by evaporation of graphite in an electric arc, we found that trichloroethylene has a somewhat higher selectivity to C_{60} than toluene. This may be connected with the fact that trichloroethylene forms a rather stable solvate with C_{60} of the composition $C_{60} \cdot C_2HCl_3$. The structure of this solvate and its thermal characteristics will be described elsewhere.

The starting reagents were mixed at 75 °C and kept at this temperature for 2 h. Then the liquor was filtered and the mother liquor was cooled at a rate of ≈1.0 deg · h^{-1} from 70 °C to room temperature. The crystals formed (black, well-cut 3-mm bars) were filtered off, washed with ethanol, and dried *in vacuo*. X-ray single crystal, microprobe, and IR spectral data showed that the solvent (trichloroethylene) was not incorporated in the crystals of the C_{60}—sulfur complex.

The crystal structure of $C_{60} \cdot 2S_8$ was determined at room temperature. Crystal data: $C_{60}S_{16}$, M = 1233.68, monoclinic, space group $C\,2/c$, T = 296 K, a = 20.90(1), b = 21.10(1), c = 10.537(9) Å, β = 111.29(7)°, V = 4331.0 Å^3, Z = 4, d_{calc} = 1.89 g · cm^{-3}, F(000) = 1824, μ = 7.66 cm^{-1}. The intensities of 1304 independent non-zero reflections with $I > 3\sigma(I)$ were measured on a crystal (dimensions 0.50 × 0.01 × 0.01 mm) on an automatic four-circle KM-4 KUMA

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Table 1. Atomic coordinates ($\times 10^4$) and B_{eq} in $C_{60} \cdot 2S_8$ structure

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$	Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
S(1)	4057(1)	4656(1)	1803(2)	11.4	C(12)	955(7)	5914(6)	−3487(13)	18.4
S(2)	3927(1)	3698(1)	1655(2)	11.4	C(13)	504(6)	6707(4)	−5280(10)	13.4
S(3)	2922(1)	3481(1)	1334(2)	10.6	C(14)	−92(6)	7706(4)	−5605(9)	11.1
S(4)	2379(1)	3416(1)	−0706(2)	10.4	C(15)	1724(6)	6553(9)	−1287(14)	19.8
S(5)	1914(1)	4272(1)	−1289(2)	9.9	C(16)	1096(6)	6441(6)	−4050(13)	15.4
S(6)	2459(1)	4741(1)	−2264(2)	10.5	C(17)	514(6)	7360(5)	−5273(9)	12.0
S(7)	3076(1)	5372(1)	−0914(2)	10.6	C(18)	1711(6)	7060(14)	−2137(22)	27.5
S(8)	4018(1)	4970(1)	−37(2)	10.1	C(19)	1457(5)	7093(9)	−3369(15)	19.5
C(1)	256(15)	5397(4)	−2483(56)	21.5	C(20)	1613(5)	7356(11)	16(11)	20.0
C(2)	855(10)	5820(7)	−290(17)	19.3	C(21)	1632(5)	7633(9)	−1273(15)	17.8
C(3)	−213(9)	5794(6)	−4798(15)	19.7	C(22)	1085(5)	7589(6)	−4154(11)	13.7
C(4)	−736(7)	6728(7)	−6010(9)	13.6	C(23)	1199(5)	7693(6)	469(10)	13.3
C(5)	1183(8)	6368(12)	0433(18)	16.6	C(24)	1279(7)	8166(8)	−2013(17)	17.7
C(6)	960(9)	5655(5)	−1608(21)	23.5	C(25)	1015(6)	8094(8)	−3480(13)	16.2
C(7)	385(11)	5664(6)	−3878(25)	26.6	C(26)	830(7)	8268(5)	−279(12)	14.8
C(8)	−78(8)	6373(4)	−5620(10)	14.7	C(27)	933(11)	8422(7)	−1361(14)	17.4
C(9)	−718(5)	7366(6)	−6004(9)	12.2	C(28)	378(9)	8439(5)	−3824(16)	16.4
C(10)	1607(8)	6700(12)	−5(21)	20.0	C(29)	139(9)	8242(5)	−158(12)	13.2
C(11)	1428(7)	6044(7)	−1820(15)	20.4	C(30)	293(9)	8653(4)	−2583(20)	15.9

DIFFRACTION diffractometer (monochromatic Mo-Kα-radiation, λ = 0.7107 Å; ω-2θ scan technique, $0.035 < \sin \theta/\lambda < 0.526$ Å^{-1}). The structure was solved by the direct method and refined by a least-squares technique in full-matrix anisotropic approximation to R = 0.041 using the package of AREN-88 programs[13]. The atomic coordinates and thermal parameters are given in Table 1.

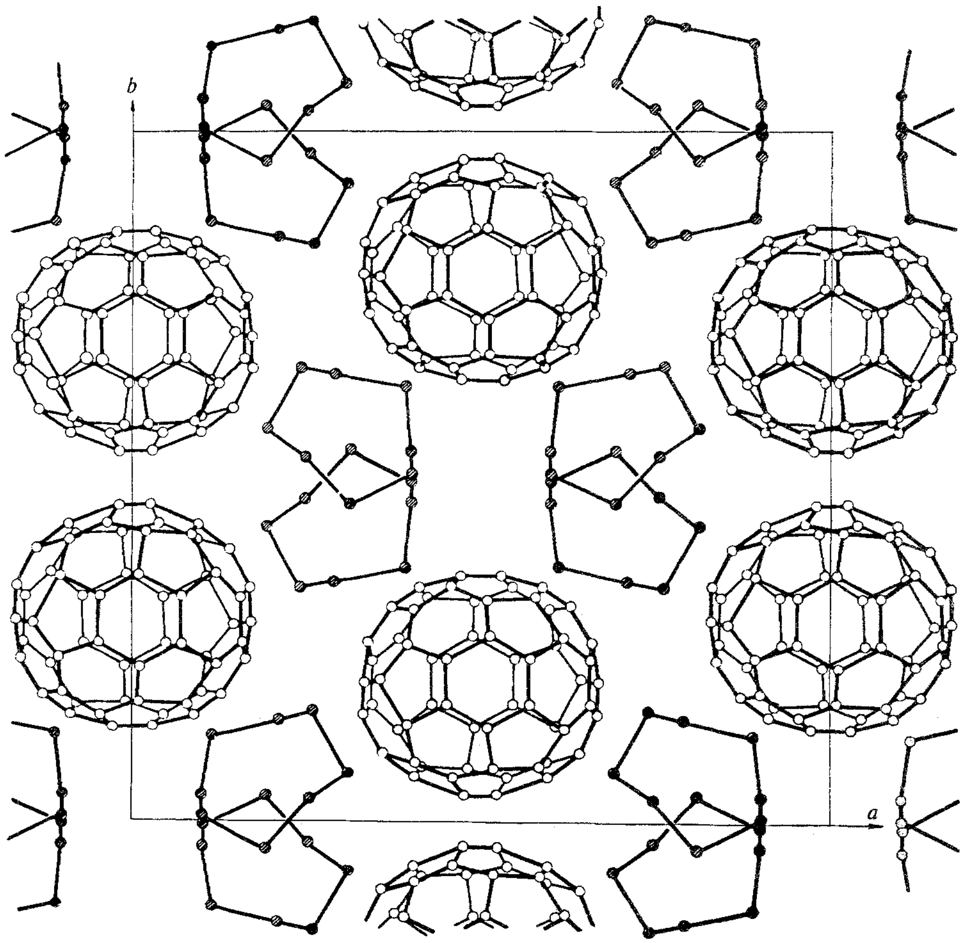

Fig. 1. Projection of the $C_{60} \cdot 2S_8$ complex structure on the *ab* plane.

Table 2. Bond lengths (*d*) in the C_{60} molecule

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
S(1)—S(2)	2.036(4)	C(17)—C(20)	1.42(1)	C(5)—C(10)	1.34(3)
S(2)—S(3)	2.052(3)	C(18)—C(21)	1.56(3)	C(7)—C(12)	1.23(2)
S(4)—S(5)	2.035(3)	C(20)—C(21)	1.49(2)	C(9)—C(14)	1.42(2)
S(6)—S(7)	2.029(3)	C(21)—C(24)	1.41(2)	C(10)—C(15)	1.49(3)
C(1)—C(1)'	1.10(5)	C(23)—C(26)	1.50(2)	C(11)—C(15)	1.26(2)
C(1)—C(7)	1.68(6)	C(25)—C(28)	1.44(2)	C(12)—C(16)	1.34(2)
C(2)—C(5)	1.41(3)	C(26)—C(29)	1.50(3)	C(13)—C(17)	1.38(1)
C(3)—C(7)	1.30(2)	C(28)—C(29)'	1.28(2)	C(14)—C(29)'	1.41(2)
C(4)—C(5)'	1.49(3)	C(30)—C(30)'	1.30(3)	C(16)—C(19)	1.61(2)
C(4)—C(9)	1.34(2)	S(1)—S(8)	2.021(3)	C(18)—C(19)	1.21(2)
C(6)—C(11)	1.36(3)	S(3)—S(4)	2.037(3)	C(19)—C(22)	1.38(2)
C(8)—C(13)	1.34(2)	S(5)—S(6)	2.046(3)	C(20)—C(23)	1.33(2)
C(9)—C(23)	1.49(2)	S(7)—S(8)	2.030(3)	C(22)—C(25)	1.32(2)
C(10)—C(20)	1.38(3)	C(1)—C(6)	1.52(3)	C(24)—C(25)	1.45(2)
C(11)—C(12)	1.69(2)	C(2)—C(3)'	1.38(3)	C(26)—C(27)	1.28(2)
C(13)—C(16)	1.54(1)	C(2)—C(6)	1.52(3)	C(27)—C(30)	1.56(2)
C(14)—C(17)	1.39(2)	C(3)—C(8)	1.58(2)	C(28)—C(30)	1.45(3)
C(15)—C(18)	1.39(3)	C(4)—C(8)	1.49(2)		

Results and Discussion

The crystal packing of C_{60} and S_8 molecules is given in Fig. 1. The C_{60} molecules are located in a unit cell on two-fold rotation axes. This packing of C_{60} leads to formation of large cavities in the form of hexagonal channels parallel to the *c* axis of the crystal. Four S_8 molecules are located in each of these cavities of the unit cell. Using the terminology of clathrate compounds, an ensemble of six fullerene molecules acts as a "host",

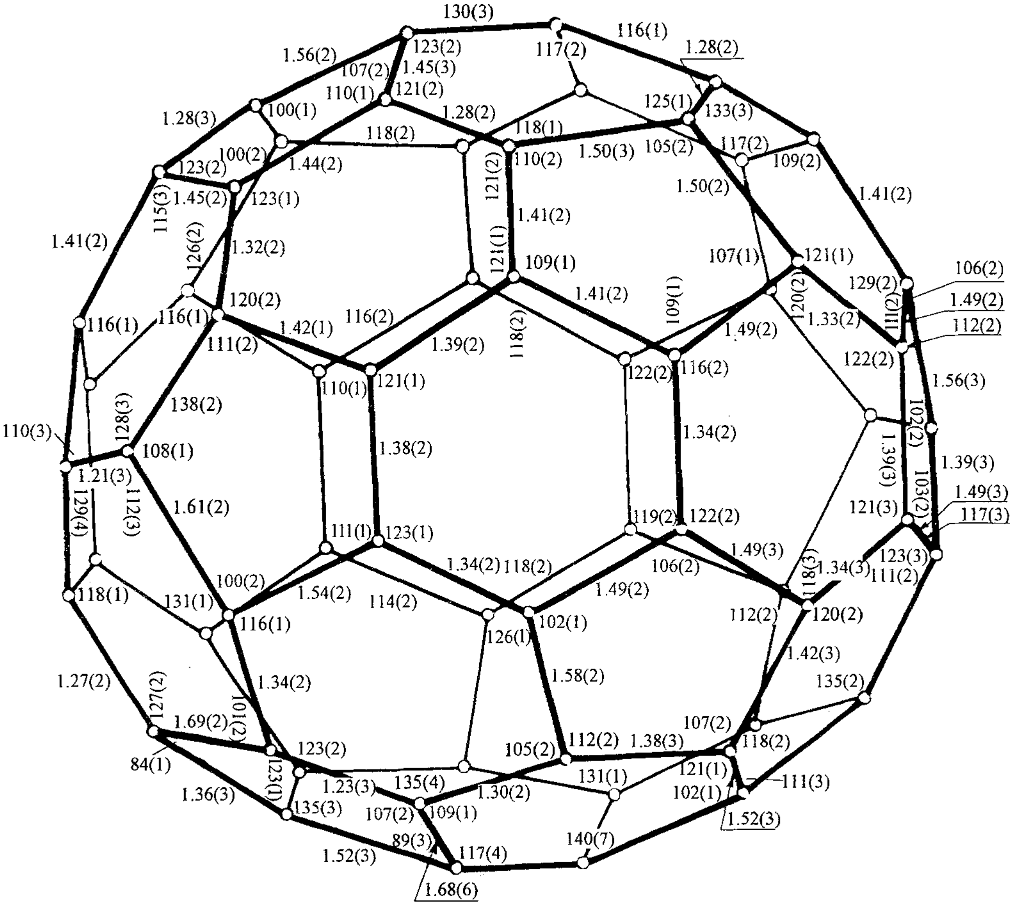

Fig. 2. Bond lengths (*d*, Å) and angles (ω, deg) of C_{60} buckminsterfullerene in the $C_{60} \cdot 2S_8$ complex.

Table 3. Bond angles (ω) in the C_{60} molecule

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
S(2)—S(1)—S(8)	107.1(2)	C(18)—C(21)—C(24)	116(1)	C(4)—C(8)—C(13)	118(2)
S(2)—S(3)—S(4)	109.5(1)	C(17)—C(22)—C(19)	111(2)	C(4)—C(9)—C(23)'	116(1)
S(4)—S(5)—S(6)	106.8(2)	C(19)—C(22)—C(25)	116(1)	C(5)—C(10)—C(15)	123(3)
S(6)—S(7)—S(8)	108.0(3)	C(20)—C(23)—C(26)	121(1)	C(20)—C(10)—C(15)	103(2)
C(6)—C(1)—C(7)	89(3)	C(21)—C(24)—C(25)	115(2)	C(6)—C(11)—C(12)	84(1)
C(7)—C(1)—C(1)'	117(4)	C(25)—C(24)—C(27)	123(2)	C(7)—C(12)—C(11)	123(1)
C(5)—C(2)—C(3)'	107(2)	C(22)—C(25)—C(28)	123(1)	C(11)—C(12)—C(16)	101(2)
C(7)—C(3)—C(8)	105(2)	C(23)—C(26)—C(27)	117(2)	C(8)—C(13)—C(17)	123(2)
C(8)—C(3)—C(2)'	112(2)	C(27)—C(26)—C(29)	125(1)	C(9)—C(14)—C(17)	118(2)
C(8)—C(4)—C(5)'	106(2)	C(24)—C(27)—C(30)	100(1)	C(17)—C(14)—C(29)'	121.5(9)
C(2)—C(5)—C(4)'	112(2)	C(25)—C(28)—C(29)'	118(1)	C(15)—C(18)—C(21)	102(1)
C(2)—C(5)—C(10)	119(2)	C(30)—C(28)—C(29)'	121(1)	C(16)—C(19)—C(18)	112(3)
C(2)—C(6)—C(11)	111(2)	C(26)—C(29)—C(28)'	117(1)	C(18)—C(19)—C(22)	128(3)
C(1)—C(7)—C(12)	107(2)	C(27)—C(30)—C(28)	107(2)	C(10)—C(20)—C(23)	122(2)
C(3)—C(7)—C(12)	135(4)	C(28)—C(30)—C(30)'	123(1)	C(18)—C(21)—C(20)	106(2)
C(3)—C(8)—C(13)	126(1)	S(1)—S(2)—S(3)	109.6(2)	C(20)—C(21)—C(24)	129(2)
C(4)—C(9)—C(14)	122(1)	S(3)—S(4)—S(5)	106.3(2)	C(17)—C(22)—C(25)	120(1)
C(23)'—C(9)—C(14)	109(1)	S(5)—S(6)—S(7)	107.1(1)	C(20)—C(23)—C(9)'	120(2)
C(5)—C(10)—C(20)	121(3)	S(1)—S(8)—S(7)	105.5(2)	C(26)—C(23)—C(9)'	107(1)
C(6)—C(11)—C(15)	135(2)	C(6)—C(1)—C(1)'	140(7)	C(21)—C(24)—C(27)	109(2)
C(15)—C(11)—C(12)	127(2)	C(5)—C(2)—C(6)	118(2)	C(22)—C(25)—C(24)	126(2)
C(7)—C(12)—C(16)	123(2)	C(6)—C(2)—C(3)'	121(1)	C(24)—C(25)—C(28)	100(1)
C(8)—C(13)—C(16)	114(2)	C(7)—C(3)—C(2)'	131(1)	C(23)—C(26)—C(29)	105(2)
C(16)—C(13)—C(17)	111(1)	C(8)—C(4)—C(9)	119(1)	C(24)—C(27)—C(26)	133(3)
C(9)—C(14)—C(29)'	109(1)	C(9)—C(4)—C(5)'	122(2)	C(26)—C(27)—C(30)	116(1)
C(15)—C(18)—C(19)	129(4)	C(10)—C(5)—C(4)'	118(3)	C(25)—C(28)—C(30)	110(1)
C(21)—C(18)—C(19)	119(3)	C(2)—C(6)—C(1)	102(1)	C(26)—C(29)—C(14)'	110(1)
C(16)—C(19)—C(22)	108(1)	C(1)—C(6)—C(11)	135(3)	C(14)'—C(29)—C(28)'	21(2)
C(10)—C(20)—C(21)	112(2)	C(1)—C(7)—C(3)	108(1)	C(27)—C(30)—C(30)'	117(1)
C(21)—C(20)—C(23)	111(2)	C(3)—C(8)—C(4)	102(1)		

while the four S_8 molecules are "guests". Each C_{60} molecule is bound to eight S_8 molecules with ten slightly shortened intermolecular contacts C...S 3.41(1)—3.52(2) Å, which attests to the existence of three-dimensional weak intermolecular donor-acceptor interactions in the crystal.

Five molecules of C_{60} itself, along with the S_8 molecules, are the nearest neighbors of the fullerene molecule. The distances between the centers of the neighboring fullerene molecules connected by the inversion centers at 0, 1/2, 0 and 1/4, 3/4, 0 are 10.036(7) and 10.636(7) Å, respectively (Fig. 1), and 10.537(9) Å for the C_{60} molecules bound by translation along the *c* axis. Generally, the packing mode of the C_{60} molecules in the structure of $C_{60} \cdot 2S_8$ forming corrugated layers of six-membered cycles $(C_{60})_6$ with the "chair" conformation is diamond-like, with the difference that we take into consideration C_{60} molecules instead of C atoms and, as a consequence, intermolecular bonds, instead of chemical bonds. On the other hand, the C...C distance between the fullerene molecules located along the $[0\bar{1}1]$ diagonal in the structure of $C_{60} \cdot 2S_8$ is the same as between the layers in graphite: 3.34(2) and 3.35(5) Å, respectively. The mean value of the C_{60} sphere radius is 3.49(2) Å (carbon atoms are located at 3.44(2)—3.53(2) Å from the center of the molecule). Bond lengths and angles in the C_{60} fullerene molecule are given in Fig. 2 and Tables 2, 3. The mean values of the eighteen crystallographically independent C=C bonds and the thirty C—C bonds are 1.32(3) and 1.47(3) Å, while the mean values of the bond angles in the five- and six-membered cycles vary in the ranges 107.6—108.0° and 119.7—120.0° with a maximum deviation of 0.07 Å of atoms from the averaged planes in the penta- and hexagons.

The S_8 molecule is an eight-membered cycle with a "crown" conformation. The S—S bond lengths, S—S—S bond angles, and S—S—S—S torsion angles vary in the ranges 2.021(3)—2.052(3) Å, 105.5(2)—109.5(1)° and 92.9—103.8°, respectively. These differences in the parameters of bond lengths and angles significantly exceed the variation of the same parameters in the orthorhombic sulfur modification (2.047(1)—2.053(1) Å, 107.4(1)—109.01(1) and 98.1—100.9°), which confirms the conformational flexibility of the S_8 molecule in the structure of the $C_{60} \cdot 2S_8$ complex and is caused by steric factors in its packing with C_{60} fullerene. In the $C_{60} \cdot 2S_8$ crystal, the S_8 molecules form shortened intermolecular contacts not only with the C_{60} molecules, but with each other as well (S...S 3.451(3) Å).

Summarizing the most significant results of the X-ray study of the $C_{60} \cdot 2S_8$ complex, it is necessary to pay attention to the considerable degree of localization of the double and single carbon—carbon bonds (1.32(3) and 1.47(3) Å) in C_{60} and the isometric packing of the C_{60} molecules (10.036(7), 10.537(9), 10.636(7) Å) in the crystal lattice. Our investigation shows that, with the appropriate choice of the donor, it is possible to obtain charge-transfer complexes with crystallographically ordered C_{60} molecules even at room temperature. Sulfur may be a versatile donor for fullerenes. Recently, the formation of a C_{70} complex with sulfur of the composition $C_{70} \cdot 6S_8$, in which the C_{70} molecules are also crystallographically ordered, has been reported.[14]

When this investigation was completed and the results were submitted for publication, the authors of this work became aware that the structure of the $C_{60} \cdot 2S_8$ complex prepared in a different way had also been studied by other researchers.[15]

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