Fullerene and Sulfur Compounds

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A new method to synthesize fullerene and sulfur compounds, C₆₀S₁₆ and C₇₀S₁₆ compounds of about 1 mm length, has been developed. The C₆₀S₁₆ crystal is a C-centered monoclinic structure of $a = 2.0874(1)$ nm, $b = 2.1139(1)$ nm, $c = 1.05690(6)$ nm and $\beta = 111.9$ degree. The C₇₀S₁₆ compound has a primitive monoclinic structure of $a = 1.5271(2)$ nm, $b = 1.49971(7)$ nm, $c = 2.18024(9)$ nm and $\beta = 109.791(1)$ degree. The crystalline structure of these compounds is constructed by fullerene and S₈-rings. A very small amount of charge-transfer between fullerenes and sulfur rings are expected by first-principle calculation.

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1. Introduction

Fullerene and sulfur compounds, such as C₆₀S₁₆, C₆₀S₈CS₂, C₇₀S₈ and C₇₀S₄₈, have been synthesized by several methods¹⁻⁹⁾ Talyzin *et al.* synthesized C₇₀S₈ crystal by evaporating organic solvents in a sealed vessel.⁷⁾ Good quality C₆₀S₁₆ and C₇₀S₄₈ thin films were prepared by co-evaporation of fullerenes and sulfur in vacuo and by a reaction of amorphous fullerene films placed in a saturated sulfur toluene solution¹⁾. A C₆₀S₁₆ single crystal of approximately 100–200 μ m was grown by heating C₆₀ sealed with excess sulfur in an evacuated glass ampoule or by slowly evaporating a solvent from a C₆₀ and sulfur solution.⁹⁾

In the present paper, a new method to synthesize fullerene and sulfur compounds and also the structural analysis of these compounds will be introduced.

2. Experimental

Pure C₆₀ and C₇₀ powders (99%), and sulfur powder (99.8%) were dissolved in toluene and prepared 5.0×10^{-4} mol/L C₆₀, 5.0×10^{-4} mol/L C₇₀ and 0.397 mol/L sulfur, respectively. The sulfur solution in toluene was filtered to remove non-dissolved materials. Using these solutions, 1.67×10^{-4} mol/L fullerene and 0.133 mol/L sulfur toluene solutions were prepared. The concentrations of fullerenes, C₆₀ and C₇₀, and sulfur in the present solutions are about one twenty-fifth and one fourth of the saturated concentrations in toluene at the room temperature, respectively. The solutions were left in tightly sealed glass vessels and settled down for a few days at room temperature. The precipitated compounds in the solutions were collected and dried for few days to completely evaporate toluene from the crystal. The atomic structures of the compounds were determined by the single crystal X-ray diffraction analysis.

3. Results and Discussion

Figure 1 shows the optical micrographs of the glossy black precipitates synthesized in the fullerene and sulfur solutions. Chemical analysis of these compounds revealed that they contain 78.9% carbon and 21.1% sulfur, and 81.4% carbon and 18.6% sulfur, respectively. Namely, they are C₆₀S₁₆ and C₇₀S₁₆. The C₇₀S₁₆ compound is novel in the C₇₀ and sulfur system. The C₆₀S₁₆ crystal is a thin rod with the flat surface about 10 μ m to 1 mm wide and 0.2 to 2 mm long. The same morphology of the C₆₀S₁₆ compound was reported in Ref. 2). The C₇₀S₁₆ crystal is a rod with rough surfaces about 30 μ m to 1 mm wide and 0.2 to 2 mm long. According to Talyzin *et al.*,⁷⁾ a dendrite structure as it is seen in Fig. 1(b) is observed at the beginning of the formation of the C₇₀S₈ crystal and transforms to the rectangular shape.

Here, it is noted that the fullerene sulfur compounds in the previous studies were grown from the supersaturated solution by evaporating the solvents. The measured density of the C₆₀S₁₆ crystal is 1.86 ± 0.02 g/cm³ that is close to the value calculated from the previously reported monoclinic structure, 1.89 g/cm³ in Ref. 3). The measured density of the C₇₀S₁₆ is 1.914 g/cm³.

Figures 2(a) and (b) shows the FT-IR spectra of the C₆₀S₁₆ and C₇₀S₁₆ crystals, respectively. The peaks at 526, 576, 1182, 1429 and 1535 cm⁻¹ marked with the solid circles in Fig. 2(a) and at 535, 565, 577, 641, 673, 794, 1086, 1132, 1320, 1414, 1430 and 1560 cm⁻¹ marked with the open circles in Fig. 2(b) are also found in pure C₆₀ and pure C₇₀, respectively.^{10,11)} This indicates that the essential atomic structures of the fullerenes, C₆₀ and C₇₀, are maintained in these compounds. The same profiles were reported in the C₆₀S₁₆ and C₇₀S₈ crystals.^{1,10)} In their spectra, however, small peaks of toluene were also observed at about 700 cm⁻¹. This structural feature of the C₆₀S₁₆ compound was also verified by observation of a single sharp peak in the ¹³C-NMR measurement.¹²⁾ No peaks assigned to C-S bonds were observed in

Fig. 1 Optical micrographs of the present (a) $C_{60}S_{16}$ and (b) $C_{70}S_{16}$ compounds.

Fig. 2 FT-IR spectra of (a) $C_{60}S_{16}$ and (b) $C_{70}S_{16}$ compounds.

the FT-IR, NMR and Raman spectra.

The structural parameters that were determined by X-ray diffraction analysis in the present $C_{60}S_{16}$ and $C_{70}S_{16}$ single crystals are summarized in Table 1. Their atomic models are shown in Fig. 3. Sulfur atoms form crown-shaped S_8 rings which are also found in solid sulfur^{13,14)} and in the other fullerene sulfur compounds.⁶⁾

The charge transfer between C_{60} and sulfur has been investigated by the first-principle calculation method. Figure 4

Fig. 3 Structures of (a) $C_{60}S_{16}$ and (b) $C_{70}S_{16}$ compounds.

shows the atomic charge distribution for the cluster model, $C_{60}-12S_8$, since one C_{60} is surrounded by twelve S_8 -rings. The details of the calculation are described in Ref. 15). It is clearly observed that a small charge transfer of about 0.01 occurs between C_{60} and S_8 -rings in the $C_{60}S_{16}$ crystal, while it is well known that no charge transfer occurs between two C_{60} s in the crystal of pure- C_{60} .¹⁵⁾ This kind of weak interac-

Table 1 Structural parameters determined by X-ray diffraction analysis in the present $C_{60}S_{16}$ and $C_{70}S_{16}$ single crystals.

Empirical formula	$C_{60}S_{16}$	$C_{70}S_{16}$
Crystal color, habit	brown needle	black block
Crystal system	monoclinic	monoclinic
Lattice type	C-centered	primitive
Space group	C2/c (#15)	P21/c (#14)
Lattice parameters	$a = 2.0874(1)$ nm $b = 2.139(1)$ nm $c = 1.05690(6)$ nm $\beta = 111.93$ degree	$a = 1.5271(2)$ nm $b = 1.49971(7)$ nm $c = 2.18024(9)$ nm $\beta = 109.791$ degree
Z value	4	4
D_{calc}	1.894 g/cm ³	1.914 g/cm ³
Radiation	CuK α ($\lambda = 0.154178$ nm)	MoK α ($\lambda = 0.071069$ nm)
Temperature	23.0°C	−180°C
No. of reflections measured	Total: 20232 Unique: 3908 ($R_{\text{int}} = 0.087$)	Total: 47392 Unique: 8951 ($R_{\text{int}} = 0.103$)
Residuals: R; R_w	0.125; 0.288	0.147; 0.214
Residuals: R1	0.095	0.088

Fig. 4 Calculated atomic charge distribution between C_{60} and twelve S_8 -rings.

tion was expected to be due to van der Waals interaction between the fullerenes and the S_8 -rings. Since these compounds

are formed in a diluted solution, it is plausible that this interaction also occurs in the solution, and it makes the fullerene and sulfur compound. Further detailed calculation is now in progress.

4. Conclusion

The relatively large fullerene and sulfur crystals, namely $C_{60}S_{16}$ and $C_{70}S_{16}$, were synthesized from the toluene solutions. The new $C_{70}S_{16}$ compound was found. The morphology of $C_{60}S_{16}$ and $C_{70}S_{16}$ crystals were a thin rod and a dendrite, respectively.

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