



# A SERIES OF NEW MOLECULAR COMPLEXES $C_{60}(S_4N_4)_{2-x}(C_6H_6)_x$ : SYNTHESIS, X-RAY STUDY OF CRYSTAL STRUCTURE AND STRUCTURAL DISORDER

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**Abstract**—The reaction of  $C_{60}$  with tetrasulfur tetranitride donor in benzene yielded a continuous series of molecular complexes:  $C_{60}(S_4N_4)_{2-x}(C_6H_6)_x$ . The study of the crystal structure of the compound with  $x = 0.67$  reveals it to have a layered structure with alternating sheets of densely packed  $C_{60}$  molecules and the sheets of the donor and benzene molecules. A statistic disorder of  $S_4N_4$  and  $C_6H_6$  molecules in one of two positions of guest molecules was found. © 1997 Elsevier Science Ltd.

**Keywords:** fullerene  $C_{60}$ , tetrasulfur tetranitride  $S_4N_4$ , X-ray crystal structure, structural disorder

## 1. INTRODUCTION

The  $C_{60}$  compounds with organic donors of different nature were a new class of materials [1, 2]. The structure and the properties of these compounds mostly depend on the structure and redox properties of the donor component. A large size, spherical shape, and high symmetry of fullerene molecules impose strong demands on the donor component. The donor has to be quite flexible to form crystal packing where heteroatoms or aromatic substituents in the donor molecule can interact with the  $C_{60}$  molecule. Recently a great number of fullerene compounds of such type were obtained:  $C_{60}(S_8)_2$  [3, 4],  $C_{60}(P_4)_2$  [5],  $C_{60}(Cp_2Fe)_2$  [6],  $C_{60}(BEDT-TTF)_2$  [7] and others [8, 9].

Tetrasulfur tetranitride molecule,  $S_4N_4$  (Fig. 1), has a cyclic crown structure [10]. A great conformational flexibility of  $S_4N_4$  makes this molecule a convenient donor for preparing complex compounds with  $C_{60}$ .

Here we report a synthesis of a continuous series of  $C_{60}$  molecular complexes with the total composition  $C_{60}(S_4N_4)_{2-x}(C_6H_6)_x$  and X-ray structural study of  $C_{60}(S_4N_4)_{1.33}(C_6H_6)_{0.67}(I)$ .

## 2. EXPERIMENTAL

Tetrasulfur tetranitride was recrystallized from 1,2-dichloroethane. Its purity was controlled by elemental analysis and IR spectra. The synthesis was carried out by a dissolving  $C_{60}$  (30 mg) and the 4–20-fold excess of  $S_4N_4$  (24–160 mg) in benzene (50 ml). The reaction mixture was filtered and the solvent was evaporated to 3–5 ml volume under argon for 5 days. The residual

solvent was decanted from the crystals precipitated. The crystals were washed by ethanol, yield about 90%. Single crystal X-ray diffraction data were collected on a Siemens P3/PN diffractometer.†

## 3. RESULTS AND DISCUSSION

The compounds obtained are listed in Table 1. The crystals of different shape and composition were obtained depending on the excess of  $S_4N_4$  with respect to  $C_{60}$ . The content of  $S_4N_4$  in the composition of the complexes increases with the increase of  $S_4N_4/C_{60}$  ratio in the initial reaction mixture and attains the maxima value only at a large excess of  $S_4N_4$ . The content of  $C_6H_6$  decreases with the increase of the content of  $S_4N_4$ .

The unit cell of I contains 12  $C_{60}$  molecules (four molecules in the centre of symmetry, and eight molecules in general positions), 12 fully ordered  $S_4N_4$  molecules (four molecules on two-fold axis, eight molecules in general positions), and 12 positions occupied by disordered  $S_4N_4$  and  $C_6H_6$  molecules with ratio 1:2. Thus, the stoichiometric composition is close to  $C_{60}(S_4N_4)_{1.33}(C_6H_6)_{0.66}(I)$  according to the results of its crystal structure refinement.

†Crystal data:  $C_{60}S_8N_8$ ,  $M = 1521.59$ , monoclinic, space group  $C2/c$ ,  $a = 29.449(6)$ ,  $b = 17.009(3)$ ,  $c = 24.127(3)$  Å,  $\beta = 114.017(12)^\circ$ ,  $V = 11039(3)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.639$ ,  $F(000) = 5460.0$ . Mo- $K_\alpha$  radiation (graphite monochromator,  $\lambda = 0.71073$  Å,  $\mu = 0.64$  mm<sup>-1</sup>),  $T = 153(2)$  K. 5338 reflections with  $2.8 < \theta < 44^\circ$  were collected. The structure was solved by direct methods using SHELXS-86 and refined using SHELXL-93 with anisotropic thermal parameters. Hydrogen atoms were located on a difference Fourier map and refined isotropically. Finally,  $R = 13.2\%$  for 5338 observed reflections [ $F_o > 4\sigma(F)$ ]. Single crystal X-ray diffraction data for Ia were collected at 153 K on Siemens P3/PN diffractometer in the Centre for X-ray structural studies, Institute of Organoelement Compounds.

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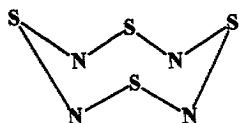


Fig. 1. Molecular structure of the donor tetrasulfur tetranitride  $S_4N_4$ .

The monoclinic crystals of I have trigonal pseudo-symmetry with three-fold pseudoaxis which passes through  $[1,0,3]$  direction. Fullerene molecules form distorted dense hexagonal layers perpendicular to  $[1,0,3]$  direction (Fig. 2). Such layered structure was previously found in  $C_{60}(I_2)_2$  [11],  $C_{60}(P_4)_2$  [5],  $C_{60}(Cp_2Fe)_2$  [6]. One third of all  $C_{60}$  molecules have eight short  $C_{60}\dots C_{60}$  contacts (six contacts within the layers and two interlayered contacts). The other two thirds of the molecules have only seven  $C_{60}\dots C_{60}$  contacts. The distances between  $C_{60}$  spheres within the layers (9.87 Å) are close to the nearest neighbouring  $C_{60}$  centre-to-centre distances in crystalline  $C_{60}$  (10.02 Å) [12]. The closest interlayered distances between the centers are 10.08 Å.  $S_4N_4$  and  $C_6H_6$  molecules are situated between  $C_{60}$  layers in the vertices of a hexagon around  $C_{60}$  molecules (Fig. 3). There are two types of guests positions in I correlated with the  $\bar{3}$  pseudoaxis. The positions of one type are occupied by the ordered  $S_4N_4$  molecules, and those of the other type are occupied by the disordered  $S_4N_4$  and  $C_6H_6$  molecules. Both types of donor positions are composed of general and special molecule locations. Average distances between the centres of  $S_4N_4$  and  $C_6H_6$  molecules and the centres of  $C_{60}$  spheres lie between 8.15–8.25 Å. Relatively high *R*-factors (13.2%) resulted from not only statistically disordered  $S_4N_4$  and  $C_6H_6$  molecules but, also due to the disorder of  $C_{60}$  molecules. This was confirmed by a wide (1.2–1.84 Å) C–C bond lengths range in the fullerene framework. Maxima of residual electron density on a difference Fourier map correspond to the second  $C_{60}$  orientation. However, the isolation of the second  $C_{60}$  orientation and the analysis of the disorder in I failed because of the small reflection.

The comparison of the average S–N bond lengths (1.58(3) Å), bond angles NSN (105(2)°) and SNS (113(2)°) in the ordered  $S_4N_4$  molecules together

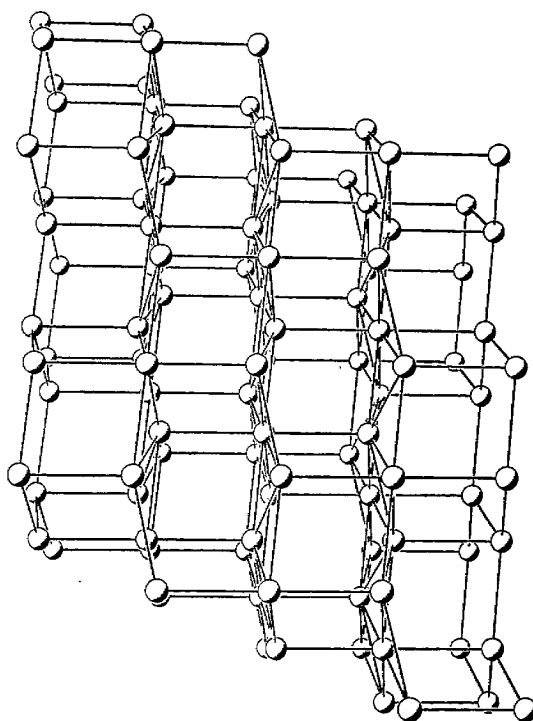


Fig. 2. Distorted dense hexagonal layers of  $C_{60}$  molecules.

coincide with those for the individual  $S_4N_4$  [10] within experimental error. Two short S...S contacts in the ordered  $S_4N_4$  of I are equal to 2.60(2) Å, which is close to those in the crystalline  $S_4N_4$  [10]. However, other four S...S contacts are equal to 2.65(2) Å, differing from those (2.71(2) Å) in crystalline  $S_4N_4$  [10]. Thus the geometric parameters of  $S_4N_4$  in Ia do not change considerably from those in pure  $S_4N_4$  allowing one to suppose only a weak charge transfer in the complex.

The crystal structure of I resembles the structures of other fullerene complexes of  $C_{60}(D)_2$  composition with a compact donor molecule:  $C_{60}(S_8)_2$  [3, 4],  $C_{60}(P_4)_2$  [5],  $C_{60}(Cp_2Fe)_2$  [6],  $C_{60}I_2 \cdot C_6H_5CH_3$  [13]. The most complexes have closely packed layers of  $C_{60}$  spheres and with usual  $C_{60}$  disorder. A weak charge transfer in this compound slightly changes the geometry of the donor molecule. But, I differs from the similar molecular  $C_{60}$  complexes by the statistic disorder of some positions of  $S_4N_4$  and  $C_6H_6$  molecules.

Table 1. The continuous series of molecular complexes of  $C_{60}(S_4N_4)_2-x(C_6H_6)_x$ , obtained in benzene

The ratio of $S_4N_4/C_{60}$ in reaction mixture $n:1$	The content of $S_4N_4$	Elemental analysis				The shape of the crystals
		C	H	N	S	
> 20	1.3	The composition was solved by solved crystal structure				Polyhedrons
20	1.0	Found	79.3	0.5	5.5	Plates
		Calc.	80.0	0.6	6.0	
10	0.9	Found	81.2	0.8	5.5	Flat hexahedrons
		Calc.	81.4	0.7	5.5	
4	0.8	Found	78.6	0.5	4.2	Flat rhomboids
		Calc.	83.5	0.7	4.6	

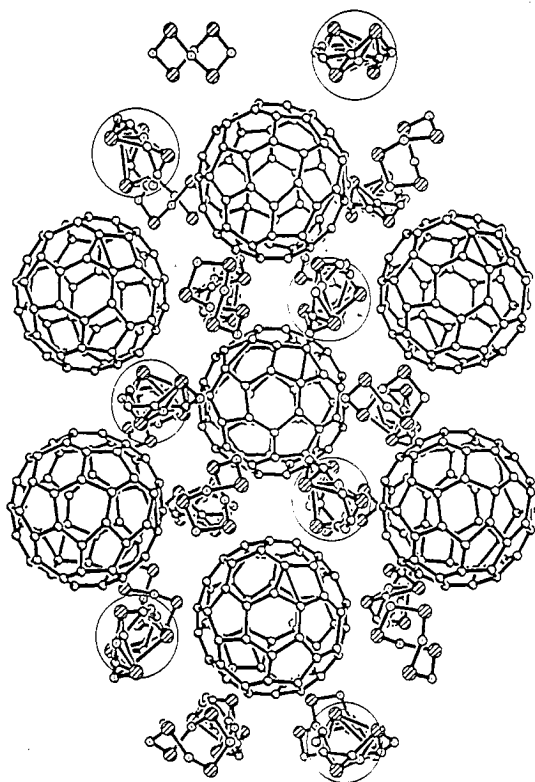


Fig. 3. The positions of  $S_4N_4$  and  $C_6H_6$  molecules are located in the vertices of the hexahedron around the  $C_{60}$  molecules. The positions in the circles are occupied by the disordered  $S_4N_4$  and  $C_6H_6$  molecules. The other positions are occupied by the ordered  $S_4N_4$  molecules.

The parameters of the unit cell of some other complexes of this continuous series  $C_{60}(S_4N_4)_{2-x}(C_6H_6)_x$  with different  $x$  are similar to those obtained for I and apparently have similar structures but differ only in the  $S_4N_4/C_6H_6$  ratio. This results from the mutual substitution of  $S_4N_4$  and  $C_6H_6$  molecules. Such substitution can occur in positions occupied by disordered molecules and associated with the close size and shape of  $S_4N_4$  and  $C_6H_6$ . For example, toluene molecules cannot be involved in complex structure and the complexes without toluene:  $C_{60} \cdot S_4N_4$  and  $C_{60}(S_4N_4)_2$  [14, 15] was obtained in toluene solution. The limiting stoichiometry of this series  $C_{60}(S_4N_4)_2$  probably cannot be reached in benzene solution, because the utilisation of large excess of  $S_4N_4$  is limited by its solubility in benzene. The compounds with a precise composition  $C_{60} \cdot S_4N_4 \cdot C_6H_6$  probably will be more ordered than the other complexes of the series. In this case the  $S_4N_4$  and  $C_6H_6$  molecules of each kind can occupy only ordered positions in the structure.

#### 4. CONCLUSIONS

A series of new molecular complexes of the total composition:  $C_{60}(S_4N_4)_{2-x}(C_6H_6)_x$  was obtained. All of them have a similar structure with disordered  $S_4N_4$  and  $C_6H_6$  molecules. The possibilities of substituting  $S_4N_4$  for  $C_6H_6$  molecules lead to the formation of the continuous series of compounds with different  $S_4N_4/C_6H_6$  ratio. These compounds have a layered structure with distorted dense hexagonal sheets of fullerenes.

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