Molecular complexes of C_{60} with tetrasulfur tetranitride

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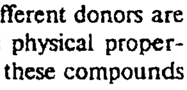
Compounds $C_{60}(S_4N_4)_{2-x}(C_6H_6)_x$ (**1a—d**) with x = 0.67 (**a**), 1.0 (**b**), 1.1 (**c**), and 1.2 (**d**), in which isomorphous replacement of S_4N_4 with benzene takes place, were obtained by the reaction of fullerene C_{60} with tetrasulfur tetranitride in benzene. Complexes $C_{60} \cdot S_4N_4$ (**2**) and $C_{60}(S_4N_4)_2$ (**3**) containing no solvent were isolated from toluene. The compositions of the compounds were established by elemental and thermogravimetric analyses. The data of IR and X-ray photoelectron (XP) spectroscopies show that in the complexes studied the transfer of electron density occurs mainly from the nitrogen atoms of S_4N_4.

Key words: fullerene C_{60}, tetrasulfur tetranitride S_4N_4, molecular complexes; thermogravimetric analysis; IR and X-ray photoelectron spectroscopies; charge-transfer complexes.

Compounds of fullerene C_{60} with different donors are new materials that can possess various physical properties.[1,2] The structures and properties of these compounds depend to a great extent on the structure and redox potential of the donor component. The large size, spherical shape, and high symmetry of the fullerene molecule are reasons for special demands to a donor. Donor molecules must be fairly flexible or have a steric structure that allows their heteroatoms or aromatic substituents to react with a molecule of C_{60}. At this time, fullerene complexes with heteroaromatic compounds,[3—6] ferrocene,[7] and several simple substances, such as S_8 [8,9] and P_4,[10] have been obtained. It is known[8] that the $C_{60}(S_8)_2$ complex crystallizes in monoclinic syngony, and S_8 molecules fill the hexagonal channels in the lattice formed by C_{60} molecules. In $C_{60}(P_4)_2$, layers of C_{60} alternate with layers of P_4.[10] According to the data of IR and XP spectroscopies, the charge transfer in these compounds is negligible.[11]

A molecule of tetrasulfur tetranitride has a cyclic crown-like structure[12] similar to that of S_8. Both addition reactions and the formation of adducts with strained olefins[13] or dienes[14] are typical of S_4N_4. Due to its ability to form adducts and its high conformational flexibility, S_4N_4 is a convenient donor for preparing of complex compounds with fullerene C_{60}. In this work, complexes of C_{60} with S_4N_4 were synthesized, their single crystals were obtained, and some physicochemical properties of the compounds isolated were studied.



Experimental

Tetrasulfur tetranitride was recrystallized from 1,2-dichloroethane; its purity was monitored by IR spectroscopy and elemental analysis.

Complexes of C_{60} with tetrasulfur tetranitride (general procedure). C_{60} and excess S_4N_4 were dissolved in benzene or toluene with heating, the reaction mixture was filtered, and the solvent was evaporated to 3—5 mL in an atmosphere of argon. The remaining solvent was decanted from the crystals that precipitated, which were washed with ethanol.

Compounds $C_{60}(S_4N_4)_{2-x}(C_6H_6)_x$ (1a—d) were obtained by evaporation of a solution of C_{60} (30 mg) and S_4N_4 (24—160 mg) (3—20-fold excess of S_4N_4 with respect to C_{60}) in benzene (50 mL) for a period of 5 days. Crystals of different shapes (black-brown to be translucent) depending on the amount of excess S_4N_4 form in a yield up to 90%.

Compounds **1a—d** isolated from benzene are characterized in Table 1. When the S_4N_4/C_{60} ratio in the initial mixture is increased, the content of S_4N_4 in the composition of the complex increases and reaches a maximum value only when the amount of excess tetrasulfur tetranitride is large

Evaporation of a solution of C_{60} (30 mg) and S_4N_4 (30.5 mg, fourfold excess) in toluene (30 mL) for a period of 20 days resulted in the formation of **$C_{60} \cdot S_4N_4$ (2)** as rhombic plates (black-brown to be translucent) in 60% yield and **$C_{60}(S_4N_4)_2$** (**3**) as bulky prisms in 30% yield. Compounds **2** and **3** were separated visually by the crystal shape. For $C_{60} \cdot S_4N_4$ (**2**) found (%): C, 77.51; H, <0.3; S, 14.41; N, 6.34. $C_{60}N_4S_4$. Calculated (%): C, 79.79; S, 14.06; N, 6.15. For $C_{60}(S_4N_4)_2$ (**3**) found (%): C, 67.05; H, 0.3; S, 23.00; N, 10.02. $C_{60}N_8S_8$. Calculated (%): C, 66.37; S, 23.40; N, 10.23.

The attempt to isolate individual compounds **2** and **3** by faster evaporation of the solvent (less than 5 days) was unsuccessful.

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Table 1. Compounds of the $C_{60}(S_4N_4)_{2-x}(C_6H_6)_x$ series obtained from benzene

Compound	n[a]	x	$\frac{\text{Found}}{\text{Calculated}}$ (%)				Crystal shape
			C	H	N	S	
1a	>20	0.67[b]	—	—	—	—	Polyhedra
1b	20	1.0	79.3 80.0	0.5 0.6	5.5 6.0	13.5 13.4	Plates
1c	10	1.1	81.2 81.4	0.8 0.7	5.5 5.5	12.4 12.4	Hexahedra
1d	4	1.2	78.6[c] 83.5	0.5 0.7	4.2 4.6	11.2 11.2	Planar rhombi

[a] The S_4N_4/C_{60} ratio in the initial mixture for synthesis of the complexes.

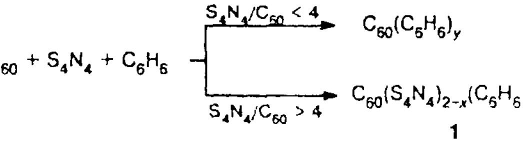
[b] From the X-ray diffraction analysis data.

[c] The content of carbon in C_{60} compounds on combustion can often be lowered. The composition was calculated from the more exact data on S and N.

Thermogravimetric analysis was carried out on a Q-1000 derivatograph in the 298—1273 K temperature range (the heating rate was 10 K min^{-1}) in quartz crucibles in an argon flow. The temperature of the exoeffect was determined from the minimum on the DTA curve, and the endoeffect temperature was determined from the beginning of a maximum on the DTA curve. IR spectra were recorded on a Specord 75 IR spectrophotometer in pellets with KBr. X-ray photoelectron spectra were recorded on a VIEE-15 instrument and calibrated by the C1s peak (285.0 eV). The resistance of single crystals was measured by the double-contact method.

Results and Discussion

When benzene solutions of S_4N_4 and C_{60} are evaporated, two competing reactions occur:



With excess S_4N_4, the equilibrium is shifted to the formation of complexes **1**. More than a fourfold excess of a donor with respect to fullerene is required for the reaction in benzene.

The thermogravigram of the decomposition of $C_{60}(S_4N_4)_{0.9}(C_6H_6)_{1.1}$ (**1c**) is presented in Fig. 1. Judging from the TG and DTG curves of complex **1c**, mass losses occur in five temperature intervals. At 353—373 K 0.4% of the total mass is lost, which probably corresponds to removal of clathrate benzene from the complex. The endothermic effect at 403 K (which is 50 °C higher than the boiling point of benzene) is likely caused by removal of coordinationally bound C_6H_6. The exothermic effect at 443 K is accompanied by the loss of 7.2% of the mass in the 443—473 K temperature range and is associated with the decomposition of S_4N_4 into its components (N and S), because, according to the published data,[15] individual S_4N_4 exothermically decomposes when heated above 451 K. At 603—743 K 5.6% more of the mass is lost due to removal of the sulfur that remains after decomposition of S_4N_4. In the 903—1073 K temperature range, a gradual loss of 8.6% of the mass occurs, which is related to sublimation of fullerene. According to the data of elemental analysis, the sample contains only carbon after heating to 800 °C.

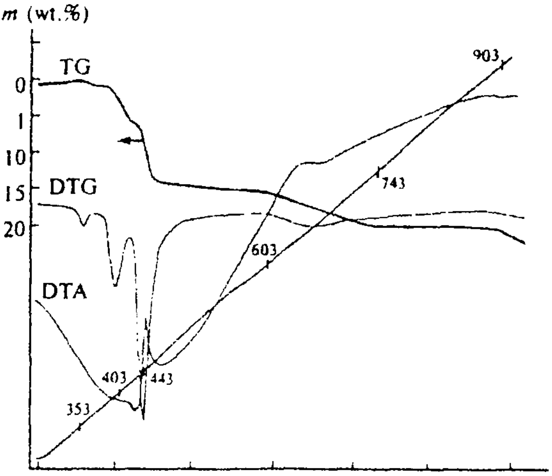


Fig. 1. Thermogravigram of the decomposition of $C_{60}(S_4N_4)_{0.9}(C_6H_6)_{1.1}$ (**1c**).

The thermogravimetric analysis of $C_{60} \cdot S_4N_4$ (**2**) showed that the mass loss occurs in three temperature intervals. The strong exothermic effect at 463 K is accompanied by mass loss (8.3%) in the 463—493 K temperature range and corresponds to decomposition of S_4N_4. All subsequent decomposition processes are similar to those described above for compound **1c**. The fact that the decomposition temperature of S_4N_4 is 20 °C higher in compound **2** than in compound **1c** is likely caused by the greater thermodynamic stability of S_4N_4 due to coordination with fullerene.

The IR spectra of compounds **1a**, **1d**, and **2** are presented in Table 2. The retention of the number of bands for C_{60} and S_4N_4 in the spectra of the complexes studied testifies that the molecular structure of their components is retained. The frequencies of the absorption bands of the vibrational modes of C_{60} change insignificantly (±1 cm^{-1}) compared to the spectrum of individual fullerene. At the same time, the spectrum of tetrasulfur tetranitride in the complexes undergoes noticeable changes. The absorption band of the degenerate stretching vibration of S—N at 925 cm^{-1} is shifted to 934 (**1a**, **1d**) and 929 (**2**) cm^{-1}. This shift of the absorption band ν(S—N) to the high-frequency region by 6—9 cm^{-1} is caused by coordination of S_4N_4 with fullerene.

Table 2. IR spectra of the initial C_{60} and S_4N_4 and complexes obtained

Compound	ν/cm^{-1}
C_{60}	1429, 1183, 576, 527
S_4N_4	925, 728, 701, 554, 548
1a*	1429, 1182, 934, 727, 701, 577, 550, 527
1d*	1429, 1182, 933, 727, 701, 576, 550, 527
2	1428, 1182, 929, 700, 577, 549, 526

* The spectrum contains additional weak absorption bands of benzene at 1478 and 674 cm^{-1}.

The relative intensity of the shoulder at 727 cm^{-1} decreases in the spectra of complexes **1a** and **1d**, and in the spectrum of **2** this shoulder disappears. The doublet of symmetric stretching vibrations of S—N (554 and 548 cm^{-1}) degenerates to a singlet at 550 cm^{-1}, which is related to lifting of the crystalline field effect,[16] since the S_4N_4 molecules are arranged fairly far from each other in the complex. The absorption bands at 1478 and 674 cm^{-1} in the spectra of complexes **1a** and **1d** are assigned to the vibrational modes of the benzene molecule. The differences in the shifts of the absorption bands of the donor for complexes **1a**, **1d**, and **2** can be associated with the different compositions and packing of molecules in the crystals.

The XP spectra of individual S_4N_4 show that the S2p peak is located between 164.6 and 164.9 eV, and the N1s peak lies between 397.8 and 398.2 eV depending on the duration of recording and the intensity of the beam of excited X-ray quanta. It was mentioned that S_4N_4 molecules desorb easily from the substrate under the conditions in which the spectra are recorded. The published values of N1s (397.9 eV) and S2p (164.5 eV)[17] for S_4N_4 are close to those obtained in this work. The XP spectra of S_4N_4 isolated in the "blank" experiment (without C_{60}) do not differ from the spectra of the initial S_4N_4. Thus, all changes in the XP spectra of S_4N_4 during complex formation are related to its reaction with fullerene.

The average values of the peaks of S2p and N1s in the XP spectra of compounds **1c** and **2** are presented in Table 3. A comparison of the binding energies of N1s and S2p for the initial S_4N_4 and for complexes **1c** and **2** shows that positive chemical shifts are observed for both peaks: 1.0—1.8 eV (N1s) and ~0.4—0.8 eV (S2p). It can be assumed that these shifts are related to the transfer of electron density from S_4N_4 to C_{60}, which occurs predominantly from the nitrogen atoms of the S_4N_4 molecule to fullerene.

The crystal structure[18] of one of the complexes of the series obtained, $C_{60}(S_4N_4)_{1.33}(C_6H_6)_{0.67}$ (**1a**), is layered (Fig. 2). Fullerene molecules form distorted com-

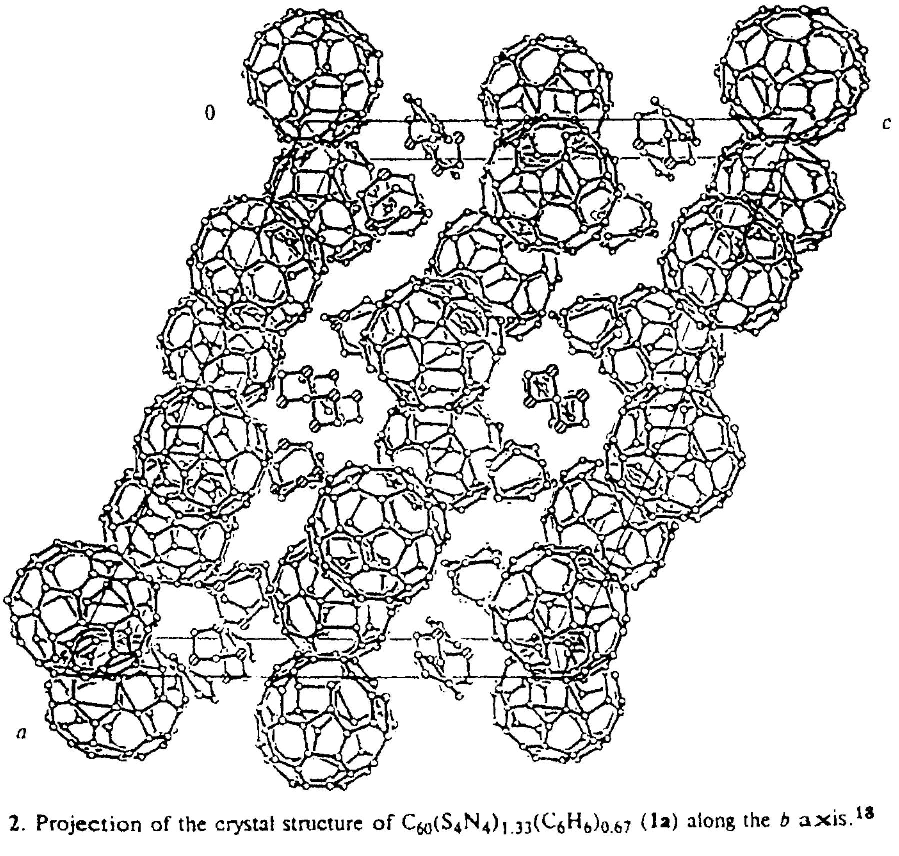


Fig. 2. Projection of the crystal structure of $C_{60}(S_4N_4)_{1.33}(C_6H_6)_{0.67}$ (**1a**) along the *b* axis.[18]

Table 3. Average values of the binding energy (eV) for S2p and N1s and positive chemical shifts (Δ/eV, relative to individual S_4N_4) in XP spectra of S_4N_4 and the complexes obtained

Compound	S2p (±0.1)	Δ (±0.2)	N1s (±0.2)	Δ (±0.4)
S_4N_4	164.75	—	398.0	—
1c	165.1	0.35	399.6	1.6
2	165.4	0.65	399.2	1.2

pact hexagonal layers with distances of 9.87 Å between centers of fullerene spheres. Molecules of S_4N_4 and C_6H_6 are arranged in cavities between the fullerene layers and occupy two different sites. One of these sites is occupied by ordered S_4N_4 molecules, and the second cavity contains disordered S_4N_4 and C_6H_6 molecules. The geometric parameters of the S_4N_4 molecules that occupy ordered sites in the structure of complex **1a**, differ only slightly from the corresponding distances and angles in crystalline S_4N_4.[12] The unit cells of complexes of the $C_{60}(S_4N_4)_{2-x}(C_6H_6)_x$ series with different x values are similar to those determined for the structure of **1a** and differ only by the ratio of S_4N_4 and C_6H_6 molecules in the crystal. This is likely related to the similar sizes of the S_4N_4 and C_6H_6 molecules, which allows them to replace each other in one of the sites of the crystal structure. The replacement is statistical and can be shifted to S_4N_4 when a great excess of tetrasulfur tetranitride is used in the initial mixture. However, the attempt to isolate the $C_{60}(S_4N_4)_2$ complex from benzene was unsuccessful due to the limit of solubility of S_4N_4 in C_6H_6.

A toluene molecule, probably due to the presence of the Me group, cannot replace S_4N_4. Therefore, complexes **2** and **3** containing no solvent were isolated from toluene. The possibility of replacing S_4N_4 with benzene in the $C_{60}(S_4N_4)_{2-x}(C_6H_6)_x$ complexes makes these structures more disordered than complex **2**.

The compounds obtained are insulators; the resistance of crystals **1b** and **1d** is $>10^7$ Ohm. No signal corresponding to $C_{60}{}^{\cdot -}$ is observed in the ESR spectra.

The transfer of the electron density from S_4N_4 to fullerene in these compounds occurs mainly from nitrogen atoms and manifests itself in shifting of the absorption bands of the stretching vibrations of the S—N bonds and positive chemical changes in the S2p and N1s peaks. No visible changes are observed in the electronic structure of the fullerene molecule, which is associated with high delocalization of the electrons in this molecule. Thus, the compounds obtained can be related to complexes with a weak charge transfer.

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