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Preparation and X-Ray Study of a Molecular Complex of C_{60} with a New Organic Cyclotetrasulfide, $4C_{60}\cdot3$(twin TDAS)

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A molecular complex of fullerene C_{60} with a new organic cyclotetrasulfide of composition $4C_{60}\cdot3$(twin TDAS) has been obtained and studied by X-ray crystallography at room temperature.

Fullerene C_{60} forms weak charge-transfer complexes (CTC) with organic donors. These complexes are stable and some of them [with $C_6H_4(OH)_2$, BEDT–TTF, twin BEDT–TTF, $(C_5H_6)_2$Fe donors] have been prepared as single crystals.[1–4] An analysis of the C_{60} CTC structures have shown the donor molecule geometry to produce a significant effect on the stability of these complexes and their packing in the crystals.[2,3] Those donors capable of changing their conformation, adapting it to a rigid spherical C_{60} shape, seem to be more able to form CTC with fullerenes.[5] In this respect, the molecules containing heterocycles linked by flexible polysulfide bridges are of special interest as donor components of the CTC with C_{60}. Thus, the presence of $–S–CH_2–CH_2–S–$ bridges in the twin BEDT–TTF molecule promotes formation of a cavity between the planar donor fragments in which a C_{60} molecule is incorporated to form a complex with twin BEDT–TTF.[2] It should also be noted that C_{60} readily forms complexes with elemental sulfur (S_8).[5–8] In this case the bond lengths and angles in the crown-shaped S_8 ring undergo marked changes in the $C_{60}\cdot2S_8$ complex as compared with the initial S_8 molecule.[5] This work reports the crystal structure and preparation of the molecular complex of C_{60} with the new organic tetrasulfide 3,3′4,4′-tetrathiobis(1,2,5-thiadiazole), $C_4N_4S_6$ (twin TDAS).

The initial twin TDAS was obtained by oxidation of a dianionic complex $[Ni(TDAS)_2]$[9,10] with hydrogen peroxide in MeCN with small additions of acetic acid. Upon standing, white needle-like crystals of twin TDAS [m.p. 233–236 °C, *m/z* 296 (M^+)] precipitated from the solution.

Hot solutions of pure C_{60} (> 98.5%) (7.2 mg, 0.01 mmol) in toluene (15 ml) and of twin TDAS (6.0 mg, 0.01 mmol) in benzonitrile (15 ml) were mixed at 100 °C and allowed to stand at this temperature for 20 min before being cooled to room temperature. Within three weeks irregular shaped black crystals appeared on the flask bottom as a result of slow evaporation of the solvent. These crystals were filtered off, washed with toluene and ether and dried in air. X-Ray analysis showed them to be of composition $4C_{60}\cdot3$(twin TDAS).[†]

The crystal structure of $4C_{60}\cdot3$(twin TDAS) (Fig. 1) is of a clathrate type. It involves packing of one basic C_{60} molecule localized in the general position and three crystallographi-

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[†] *The main crystal data*: $C_{252}N_{12}S_{18}$. $M = 3771.72$, $a = 19.007(8)$, $b = 19.024(9)$, $c = 18.991(7)$ A, $V = 6867(2)$ A , space group I222, $Z = 2$, $D_c = 1.82\ \mathrm{g\,cm^{-3}}$, $F(000) = 3768$. The intensities of 2341 non-zero reflections [among them 1568 reflections with $F > 4\sigma(F)$ were used to solve the structure] were measured on a four-circle automatic KM-4 KUMA DIFFRACTION diffractometer, MoKα-radiation, θ-2θ scan technique over the range of angles with $(2\theta)_{max} = 44.07°$. The atomic positions in three crystallographically-independent twin TDAS molecules were revealed by direct methods using the SHELX-86 program.[11] The atomic coordinates in the C_{60} fullerene molecule were determined by a series of successive difference Fourier syntheses that alternated with refinement by a least-squares technique in isotropic approximation of the positions of localized atoms. The final refinement of the $4C_{60}\cdot3$(twin TDAS) structure was performed with full-matrix least-squares in anisotropic approximation for all atoms to $R = 0.048$ using the SHELXL-93 program.[12] No correction for absorption was applied ($\mu_{MoK\alpha} = 0.37\ \mathrm{mm^{-1}}$). The weighting scheme was $w = 1/[\sigma^2F^2_{obs} + (0.1233P)^2 + 10.86P]$, where $P = [(\max F^2_{obs}) + +2F^2_{calc}]/3$. Atomic coordinates, bond lengths, bond angles and torsion angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *Mendeleev Commun.*, 1994, issue 1.

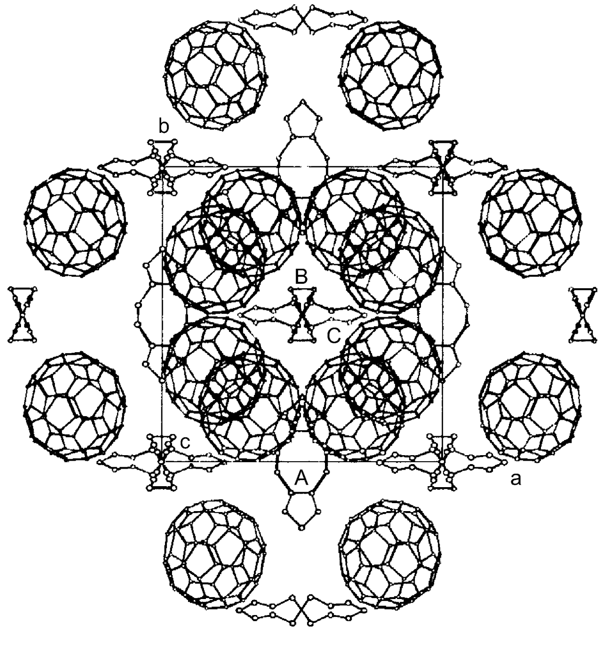

Fig. 1 The crystal structure of the $4C_{60}{\cdot}3$(twin TDAS) complex.

cally-independent twin TDAS molecules (denoted as A, B and C) localized in special positions. As a result eight spherical molecules C_{60} are arranged in the quasicubic unit cell so as to form cavities and channels in the crystal lattice. The cavities are located on the cell faces and the channels are parallel to the *c* axis and go through the beginning (0,0,0) and the middle $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ of the unit cell. Each cavity is formed by four C_{60} molecules and is of a tetrahedral configuration in which a propeller-shaped tetrasulfide A molecule fits as a key in the lock. Each channel inside the unit is formed by eight C_{60} molecules. The cross-section is rhombic which is obviously most favourable for the two guest tetrasulfide molecules B and C oriented along and across the channel axis to be included in the channel. Thus, regardless of the location of the twin TDAS molecule – in the cavity or in the channel – it is symmetrically surrounded by four C_{60} molecules. As an analysis of the intermolecular distances has shown, it forms with their C=C groups eight slightly shortened N···C contacts (Fig. 2). Respectively, each C_{60} molecule forms six shortened C···N contacts with the nearest three twin TDAS molecules. In addition, each C_{60} molecule has three shortened contacts C···C 3.19.2–3.31(3) A with three neighbouring fullerene molecules. The distances between the centres of the fullerene molecules in contact are 10.07, 10.10 and 10.11 A. We assume that the intermolecular interactions $C_{60}\cdots C_{60}$ and $C_{60}\cdots$(twin TDAS) do in fact completely stop the rotation of the fullerene molecules themselves, which allowed us to carry out this X-ray crystallographic investigation at room temperature.

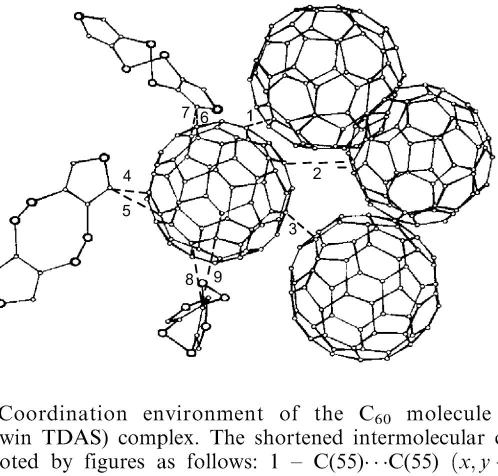

Fig. 2 Coordination environment of the C_{60} molecule in the $4C_{60}{\cdot}3$(twin TDAS) complex. The shortened intermolecular contacts are denoted by figures as follows: 1 – C(55)···C(55) $(x, y-1, -z)$ 3.28(2) A; 2 – C(9)···C(9) $(-x, 1-y, z)$ 3.31(2) A); 3 – C(11)···C(11) $(-x, y, -z)$ 3.19(2) A; 4 – N(1)···C(30) 3.25(2) A; 5 – N(1)···C(31) 3.25(2) A; 6 – N(2)···C(19) 3.25(2) A; 7 – N(2)···C(20) 3.25(2) A; 8 – N(3)···C(39) 3.27(2) A; 9 – N(3)···C(47) 3.25(2) A.

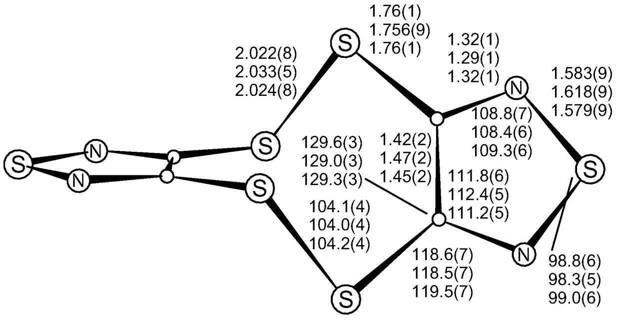

Fig. 3 Propeller conformation, bond lengths/A and angles/° in twin TDAS molecules A (upper line), B (middle line), C (lower line).

The molecules of twin TDAS tetrasulfides have a propeller conformation with crystallographic symmetry 222. The lengths of chemically equivalent bonds and the angles in the molecules A, B and C (Fig. 3) coincide within the estimated standard deviations. The five-membered heterocycles are in fact planar. The maximum deviations of the atoms from the mean planes of the rings are 0.005 A for the A molecule, 0.014 A for the B and 0.009 A for the C molecules. The mean planes of the TDAS fragments in the molecules A, B and C are turned relative to each other and form dihedral angles of 50.1, 51.1 and 51.2°, respectively.

The conformations, interatomic distances and angles in the twin TDAS 3.4-dithiothiadiazole fragments of the $4C_{60}{\cdot}3$(twin TDAS) complex are the same as analogous fragments in the previously investigated nickel complexes $(RN)_2[Ni(TDAS)_2]$, where R = Et_4,[10] Bu_4,[10] $Me(C_8H_{17})_3$. Differences are only found in the S–N and S–C bonds. In the $4C_{60}{\cdot}3$(twin TDAS) complex, the S–N bonds are, on average, 0.08 A shorter and the C–S bonds are 0.04 A longer than in the nickel complexes, which may be connected with different charge states of the 3,4-dithiothiadiazole fragments. The S–S bonds in the molecules of A, B and C are slightly shorter than in the other cyclic polysulfides C_3S_8,[13] C_6S_{12}[14] and $C_6S_{10}{\cdot}(CS_2)_{0.5}$,[15] but correspond to the lower boundary of the 2.021(3)–2.052(3) A range in the $C_{60}{\cdot}2S_8$ complex.[5]

The fullerene C_{60} molecule has an approximately spherical form: the average distance between the C atoms and the molecule centre of gravity $R_{av} = 3.51$ A, while the interval of all these distances varies from $R_{min} = 3.45$ A to $R_{max} = 3.56$ A. As noted above, the C_{60} molecule is in the general position, which allowed us to calculate the lengths of all the 30 inter-pentagonal "double" (C=C) bonds and all the 60 intra-pentagonal "single" (C–C) bonds. An analysis of the interatomic distances has shown that the C=C bonds vary from 1.09(3) to 1.49(3) A with an average length $(C{=}C)_{av}$ of 1.31(4) A. The analogous values for the C–C bonds are: $(C\text{–}C)_{min} = 1.31(3)$ A, $(C\text{–}C)_{max} = 1.67(3)$ A and $(C\text{–}C)_{av} = 1.48(4)$ A. The maximum deviation of the C atoms from the mean planes in five and six-membered rings does not exceed 0.04 A. The given geometric characteristics of the C_{60} fullerene molecule in the $4C_{60}{\cdot}3$(twin TDAS) complex are close to the respective characteristics of the C_{60} fullerene in the $C_{60}{\cdot}2S_8$ complex.[5]

It should be mentioned that, in the crystal structure of the C_{60}–twin TDAS complex, as distinct from C_{60}–twin BEDT–TTF,[2] the donor plays the role of "guest" molecule. We believe that in clathrates of this type the distribution of the functions "host–guest" between the C_{60} and the donor molecules depends to a large extent on a donor's conformation. If a donor has a non-planar conformation allowing, at least partially, envelopment of the C_{60} molecule then it is probable that this donor will behave as a "host". The crystal structures of the (twin BEDT–TTF)$\cdot C_{60} \cdot CS_2$[2] and (BEDT–TTF)$_2 \cdot C_{60}$[3] complexes confirm this assumption.

The propeller conformation of the twin TDAS differs significantly from the U-shaped conformation of the twin BEDT–TTF[2] and the chair conformation of the twin DMIT.[15] An effective complex formation for C_{60} and twin TDAS is probably reached owing not only to charge-transfer interactions, but also because of the flexibility of the twin TDAS molecule. Because of the presence of sulfide bridges the latter may change its geometry, adapting it to the size and shape of the channels and cavities in the C_{60} lattice of the crystal structure.

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