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Brief Communications

Crystal structures of molecular complexes of fullerene C_{60} with tetraphenylsilane and tetraphenylgermane

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New molecular complexes of fullerene $C_{60} \bullet Ph_4E$ (E = Si, Ge, and Sn) were synthesized, and their crystal structures were determined. All molecular complexes are isostructural single-phase systems. The planes of the benzene rings in the Ph_4E molecules are virtually parallel to the six-membered fragments of the fullerene molecule.

Key words: X-ray diffraction study, fullerene, tetraphenylsilane, tetraphenylgermane, tetraphenylstannane, molecular complex, structure.

Neutral molecular complexes of fullerene with π-donor organic and organometallic compounds have attracted attention because these complexes have wide application in the synthesis of new composite and functional materials.[1–5]

The physical properties of these complexes are greatly determined by their structure. The packing of fullerene molecules and the distances between the molecules in the crystal structures depend on the structure and properties of the incorporated donor molecules. Hence, to prepare materials with desired properties based on molecular complexes of fullerene, it is of importance to know the structural features of these compounds.

In the present study, to examine the possibility of preparing composite materials based on fullerene and organic compounds of Group 14 elements, we synthesized new molecular complexes of fullerene C_{60} with tetraphenylsilane, tetraphenylgermane, and tetraphenylstannane. The crystal structure of Ph_4Si, Ph_4Ge, and Ph_4Sn[6] is a tetragonal lattice containing a Si (Ge or Sn) atom at the origin of coordinates surrounded by four benzene rings in such a way that there are three-dimensional cavities between the molecules, which can be occupied by fullerene molecules. In the crystal lattices of the starting tetraphenyl-substituted derivatives Ph_4E, these cavities are partially occupied by the phenyl ligands of the adjacent molecules.

The single-crystal X-ray diffraction study of the molecular complexes $C_{60} \cdot Ph_4E$ (E = Si (**1**) and Ge (**2**)) showed that complexes **1** and **2** are isostructural. In the crystal structures, the fullerene and Ph_4E molecules are located on a fourfold axis (Fig. 1).

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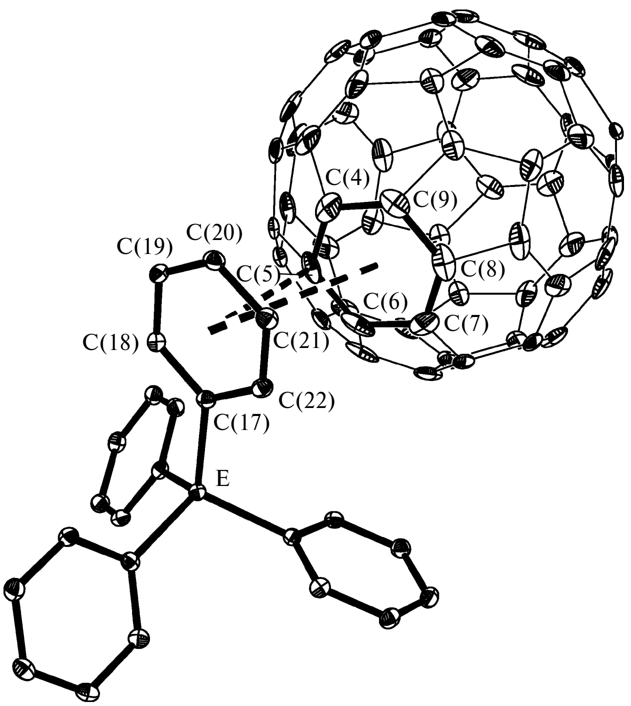

Fig. 1. Structural fragment of complexes **1** (E = Si) and **2** (E = Ge). Displacement ellipsoids are drawn at the 30% probability level. In the crystal structure, each benzene ring faces a fullerene molecule.

As a result, the five- and six-membered fragments of the fullerene molecules are disordered about the fourfold axis. It should be noted that all benzene rings in the Ph_4E molecules are virtually parallel to the six-membered moieties of the fullerene. The corresponding dihedral angle is 9.1° and 9.9° for compounds **1** and **2**, respectively. The distances between the centers of the benzene rings of the Ph_4E molecules and the corresponding fragments of the fullerene molecules are 3.806 and 3.796 Å in **1** and **2**, respectively. It is interesting that an increase in the Ge—C(Ph) distances (1.9514(13) Å) by 0.076 Å compared to the Si—C(Ph) distances (1.8751(13) Å) leads to a shortening of the distances between the centers of the benzene rings of the Ph_4Ge molecules and the centers of the six-membered fragments of the fullerene molecules by 0.01 Å. The shortest distance between the center of the benzene ring and the C(5) atom of the fullerene molecule is 3.460 and 3.451 Å in compounds **1** and **2**, respectively. Apparently, this is indirect evidence of the attractive interactions between the π-system of the phenyl ring and the fullerene molecule. If repulsive interactions between these moieties dominate, the corresponding distances would be slightly larger or would change in proportion to the E—C(Ph) bond length. An analogous situation is observed in the isostructural complexes $C_{60} \cdot Ph_4ECl$, where E is P (see Ref. 7) or As,[8] in which the phenyl groups are also virtually parallel to the six-membered fragments of the fullerene molecules. An increase in the As—C(Ph) distances by 0.095 Å compared to the P—C(Ph) distances leads to a shortening of the distances between the centers of the benzene rings of the Ph_4As molecules and the centers of the six-membered fragments of the fullerene molecules by 0.008 Å. Since the benzene rings of the Ph_4E molecules are parallel to the hexagonal fragment of the adjacent fullerene molecules, the Ph_4E and C_{60} molecules in the crystal structures of compounds **1** and **2** are arranged in a herringbone fashion parallel to the *ab* plane (Fig. 2, *a*). The layers consisting of the Ph_4E and C_{60} molecules alternate in the projection onto the *ac* plane perpendicular to the herringbone packing, the layer of C_{60} molecules having a zigzag shape (Fig. 2, *b*).

We failed to grow single crystals of $C_{60} \cdot Ph_4Sn$ (**3**) suitable for X-ray diffraction study. Hence, we studied compounds **1**—**3** by X-ray powder diffraction. Figure 3 represents the X-ray diffraction patterns of compounds **1**—**3**, which show that all molecular complexes of fullerene with the tetraphenyl-substituted derivatives Ph_4E (E = Si, Ge, or Sn) are isostructural individual phases.

Therefore, we demonstrated for the first time that it is possible to synthesize stable molecular complexes of fullerene C_{60} with organosilicon, -germanium, and -tin compounds. The introduction of fullerene molecules into

Table 1. Principal crystallographic characteristics and the X-ray data collection and refinement statistics for complexes **1** and **2**

Parameter	**1**	**2**
Molecular formula	$C_{84}H_{20}Si$	$C_{84}H_{20}Ge$
Molecular weight	1057.09	1101.59
Crystal system	Tetragonal	
Space group	P_4/n	
a/Å	12.5485(12)	12.5659(2)
c/Å	14.1432(14)	14.2098(4)
V/Å^3	2227.1(4)	2243.75(8)
Z	2	2
d_{calc}/g cm^{-3}	1.576	1.631
μ/mm^{-1}	0.116	0.745
F(000)	1076	1112
Crystal dimensions/mm	0.27×0.19×0.10	0.25×0.15×0.08
θ-Angle range/deg	2.71—26.99	1.62—27.49
hkl Ranges	$-16 \le h \le 15$	$-16 \le h \le 16$
	$-16 \le k \le 16$	$-14 \le k \le 16$
	$-18 \le l \le 18$	$-18 \le l \le 16$
Number of reflections:		
observed	19870	15082
independent	2421	2562
R_{int}	0.1444	0.0312
Goodness-of-fit (F^2)	0.942	1.006
R_1/wR_2 ($I > 2\sigma(I)$)	0.0524/0.1040	0.0367/0.0880
R_1/wR_2 (based on all reflections)	0.1045/0.1172	0.0442/0.0916
Residual electron density (ρ_{max}/ρ_{min})/e $\cdot$ Å^{-3}	0.272/–0.351	0.351/–0.254

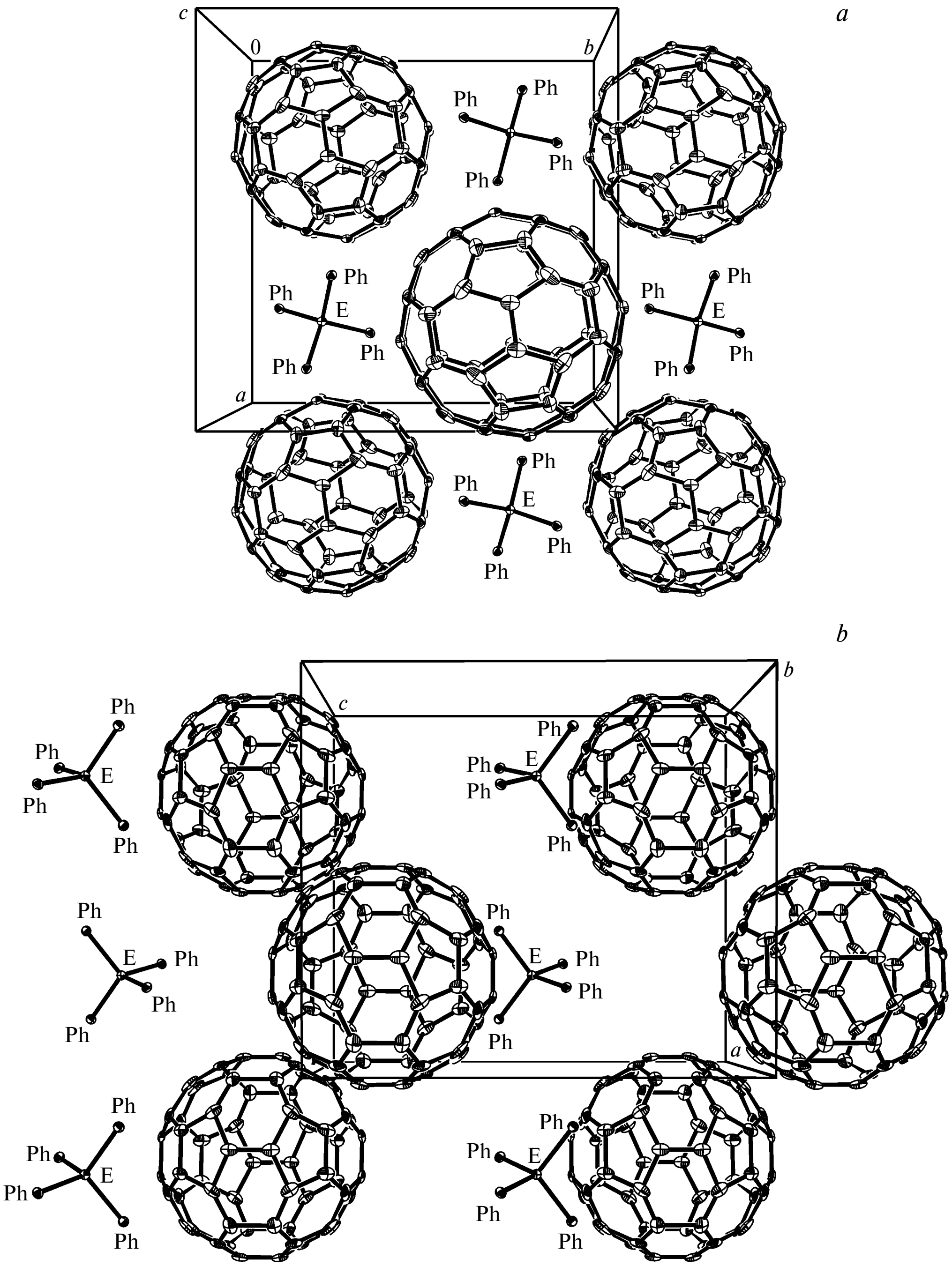

Fig. 2. Crystal packing of complexes **1** and **2** projected onto the planes *ab* (*a*) and *ac* (*b*).

the tetragonal lattice of Ph_4E results in the tetrahedral arrangement of the fullerene molecules with respect to Ph_4E. The tetrahedral arrangement of the C_{60} molecules about Ph_4E is apparently determined by weak π—π interactions between the benzene ring and the hexagonal fragment of C_{60}, which is indirectly evidenced by the virtually parallel orientation of these six-membered fragments according to the X-ray diffraction data for the crystals of compounds **1** and **2**.

Experimental

Fullerene with a purity of 99.5% was purchased from the Fullerene Center (Nizhnii Novgorod). Benzene was purified by distillation over sodium under an argon flow. Tetraphenylsilane and tetraphenylgermane were synthesized according to known procedures.[9,10]

Complexes $C_{60} \cdot EPh_4$ (E = Si, Ge, Sn) were prepared by crystallization using the slow diffusion of a saturated benzene solution of fullerene C_{60} into a saturated benzene solution of

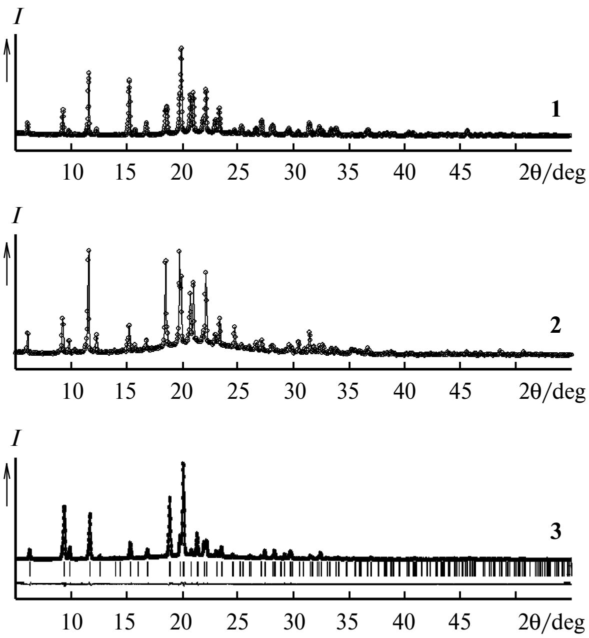

Fig. 3. Results of the refinement for $C_{60}\cdot Ph_4Si$ (**1**) and the experimental X-ray diffraction patterns for $C_{60}\cdot Ph_4Ge$ (**2**) and $C_{60}\cdot Ph_4Sn$ (**3**).

Ph_4E (E = Si, Ge, Sn) at room temperature. In all cases, the volumes of the saturated solutions were taken in a ratio of 1 : 1. The crystals precipitated after 24 h. Large single crystals of the complexes $C_{60}\cdot Ph_4E$ were grown by the slow evaporation of benzene for 2—3 weeks. Single crystals of the complexes are black sparkling well-faceted parallelepipeds; in the case of the complex with germanium, the edge sizes are up to 3—4 mm.

X-ray diffraction study. The X-ray diffraction data sets for complexes **1** and **2** were collected at 100 K on a Bruker AXS SMART APEX diffractometer (φ—ω-scanning technique, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator). Absorption corrections were applied using the SADABS program.[11] The structures of **1** and **2** were solved by direct methods using the SHELXS97 program package[12] and refined by the full-matrix least-squares method based on F^2 with the use of the SHELXL97 program package.[13] All nonhydrogen atoms were refined anisotropically. All H atoms in compound **1** were positioned geometrically and refined using a riding model. The hydrogen atoms in compound **2** were located in difference electron density maps and refined isotropically. The disordered fragments of the fullerene molecules were refined with 50% site occupancies. Principal crystallographic characteristics and the X-ray diffraction data collection and refinement statistics for complexes **1** and **2** are given in Table 1. The X-ray powder diffraction study was carried out on a DRON-3M diffractometer at $T = 293$ K using graphite-monochromatized Cu-Kα radiation in the angle range of 5—60° with a step size of 0.02°. In the X-ray diffraction patterns (see Fig. 3), the lines of the starting compounds were absent, and the products were indexed as a tetragonal phase with the criterion $M_{20} > 100$. The refinement of the peak profiles and the lattice parameters by the full-profile analysis (see Fig. 3, *a*) for the space group P_4/n gave the following unit cell parameters: $a = 12.682$ Å, $c = 14.355$ Å for complex **1**, $a = 12.699$ Å, $c = 14.411$ Å for complex **2**, and $a = 12.722$ Å, $c = 14.413$ Å for complex **3**. Some discrepancy between the unit cell parameters determined based on the powder and single-crystal X-ray diffraction data is attributed to the difference in the temperature of the X-ray data collection.

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