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Fullerene complexes with bis(η^6-hexamethylbenzene)chromium, hexamethylbenzene, and hexaethylbenzene

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The [60]fulleride of bis(η6- hexamethylbenzene)chromium(I) $[(\eta^6\text{-}C_6Me_6)_2Cr]^{\bullet+}[C_{60}]^{\bullet-}$, and the complexes $C_{60}\cdot C_6Me_6$ and $C_{60}\cdot C_6Et_6$ were synthesized. Thermal decomposition of $[(\eta^6\text{-}C_6Me_6)_2Cr]^{\bullet+}[C_{60}]^{\bullet-}$ was studied. The molecular structures of $C_{60}\cdot C_6Me_6$ and $C_{60}\cdot C_6Et_6$ were determined.

Key words: C_{60} fullerene, chromium bisarene complexes, hexamethylbenzene, hexaethylbenzene, donor-acceptor complexes, ESR, X-ray diffraction analysis, crystal structure, thermal decomposition.

In recent years, considerable attention has been focused on salt-type fullerides of bis-cyclopentadienyl and bisarene transition metal complexes.[1—7] When oxidized, the complex $(\eta^6\text{-arene})_2Cr^0$ is known[8] to give off an electron from the highest occupied molecular orbital, which is actually chromium $3d_{z^2}$ atomic orbital. It appeared pertinent to try the reaction of C_{60} fullerene with C_6Me_6 or C_6Et_6 and with the complexes $(\eta^6\text{-}C_6R_6)_2Cr^0$ (R = Me, Et). On the one hand, these complexes have the lowest ionization potentials,[9] but, on the other hand, the degree of spatial shielding of the chromium atoms by arene ligands is higher in these complexes than in $(\eta^6\text{-}C_6H_6)_2Cr^0$ (see Refs 10 and 11).

Results and Discussion

It was found that C_{60} fullerene reacts with $(\eta^6\text{-}C_6Me_6)_2Cr^0$ in toluene at room temperature to give complex **1** as a brown precipitate. Analysis of the chromium content in the molecule of **1** and in the initial complex $(\eta^6\text{-}C_6Me_6)_2Cr^0$ shows that the $(\eta^6\text{-}C_6Me_6)_2Cr^0 : C_{60}$ molar ratio in **1** is close to unity. The ESR spectrum of a solution of **1** in PhCN (Fig. 1) is a singlet with $g = 1.986$, typical of the $(\eta^6\text{-arene})_2Cr^{\bullet+}$ radical cations, and the ESR spectrum of fulleride **1** in the solid state at 290 K is a singlet with $g = 1.9919$, $\Delta H \approx 4.0$ mT. The ESR spectrum of complex **1**, like the spectra recorded previously,[1,5,6] exhibits no signal for the fullerene radical anion, apparently, since this signal is too broad.[1] Broadening of this ESR signal may be due to the reversible dimerization

$$2\,[C_{60}]^{\bullet-} \rightleftharpoons [C_{60}\text{—}C_{60}]^{2-}.$$

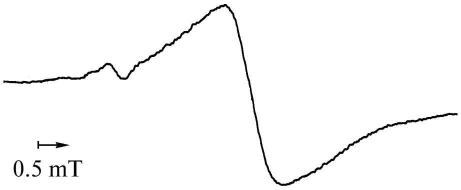

Fig. 1. ESR spectrum of complex **1** in PhCN.

The set of physicochemical properties of compound **1** indicates that this is a salt-like fulleride $[(\eta^6\text{-}C_6Me_6)_2Cr]^{\bullet+}[C_{60}]^{\bullet-}$ of the radical-ion type.

$$(\eta^6\text{-}C_6Me_6)_2Cr^0 + C_{60} \xrightarrow[PhCH_3]{293\text{ K}} [(\eta^6\text{-}C_6Me_6)_2Cr]^{\bullet+}[C_{60}]^{\bullet-}$$

It was shown by ESR spectroscopy that the sandwich bis(arene)chromium structure of the radical cation $(\eta^6\text{-}C_6Me_6)_2Cr^{\bullet+}$ in the solid sample **1** is completely destroyed in vacuum at 473 K (the ESR signal disappears).

The C_{60} fullerene reacts with C_6Me_6 and C_6Et_6 in a solution in $o\text{-}Cl_2C_6H_4$ at room temperature to give crystalline compounds **2** and **3**, respectively. The IR spectra of complexes **2** and **3** contain absorption bands typical of C_{60} fullerene and hydrocarbons. The absorption C—H bending bands in the spectrum of complex **3** (675 and 1481 cm^{-1}) are shifted toward lower frequencies by 6 and 9 cm^{-1} with respect to those in the spectrum of C_6Et_6, while the bands at 1227, 1248, and 1313 cm^{-1} are missing.

A powder X-ray diffraction study showed that each of compounds **2** (Fig. 2) and **3** has only one crystalline phase typical of the given compound, while the C_{60} fullerene phase is completely missing. According to single-crystal X-ray diffraction analysis, molecules **2** and **3** are located

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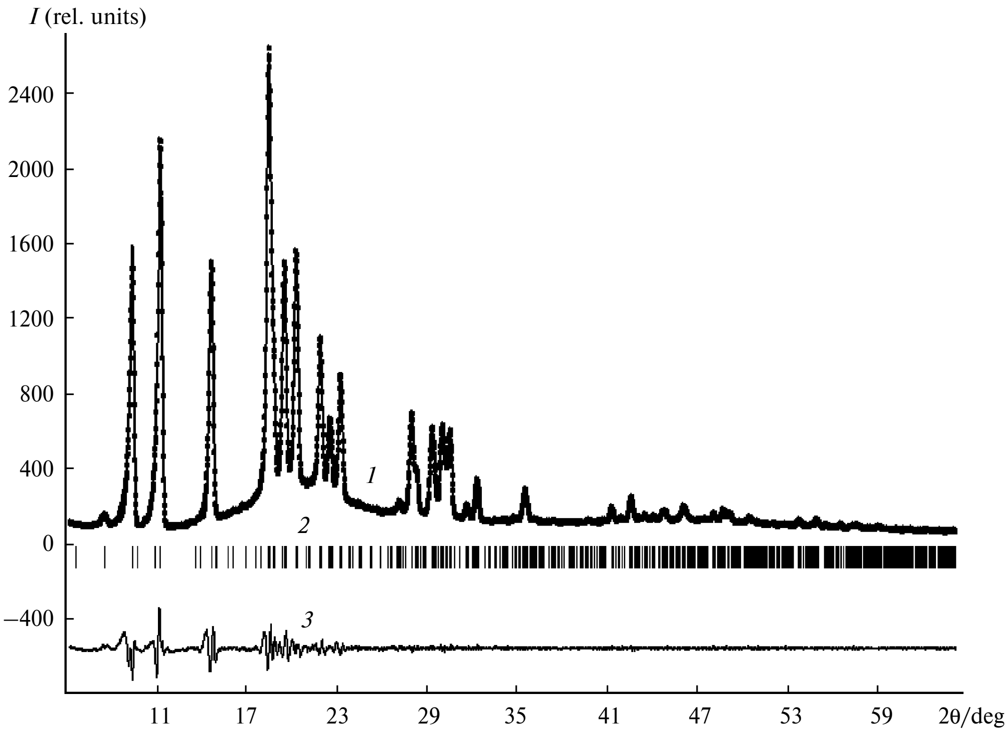

Fig. 2. Experimental (dashed line) and refined (continuous line) X-ray diffraction patterns of complex **2** (*1*), positions of the reflections (*2*), and the difference curve (*3*).

on axis 2 and on inversion axis 3, respectively, and are packed in layers formed by chains made of C_{60} and C_6R_6 in 1 : 1 ratio (Figs 3 and 4). The C_6Me_6 molecule in the crystal of **2** is arranged above the five-membered C(5)C(6)C(7)C(20)C(21) fragment (Fig. 5). The dihedral angle between them is 5.2°. The distance between the centers of the C_6Me_6 and the C(5)C(6)C(7)C(20)C(21) fragments is 3.26(1) Å. The distance between the center of the six-membered C_6Me_6 fragment and the midpoint of the C(20)—C(21) segment is the shortest, being equal to 3.16(1) Å. The C(5)...C(31), C(20)...C(32A), and C(21)...C(33A) distances are 3.29(1), 3.24(2), and 3.19(2) Å, respectively, which is much smaller than the sum of the van der Waals radii of the carbon atoms (3.4 Å).[12]

In the crystal of **3**, the C_6Et_6 molecule is located above the six-membered fragment, C(3)C(3A)C(3B)C(4)C(4A)C(4B) (Fig. 6). The rotation angle between them is 26°, the planes accommodating them being parallel to each other. The ethyl groups in the C_6Et_6 molecule occupy the *trans*-positions relative to each other. The distance between the centers of the C_6Et_6 and C(3)C(3A)C(3B)C(4)C(4A)C(4B) fragments amounts to 3.885(3) Å, which is much longer than this distance in

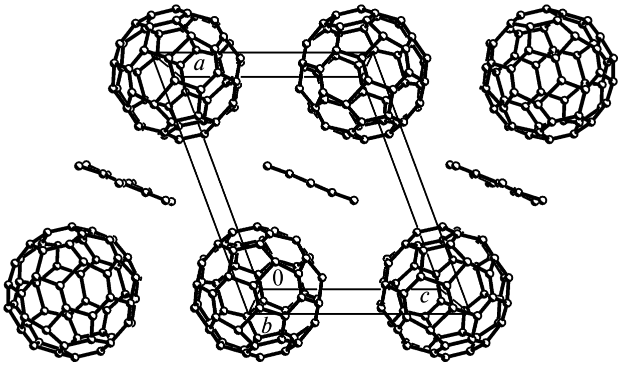

Fig. 3. Projection of the fragment of the crystal packing of complex **2** onto the *ac* plane.

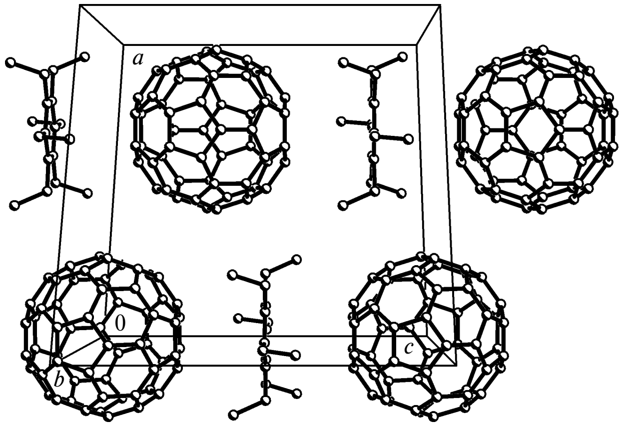

Fig. 4. Projection of the fragment of the crystal packing of complex **3** onto the *ac* plane.

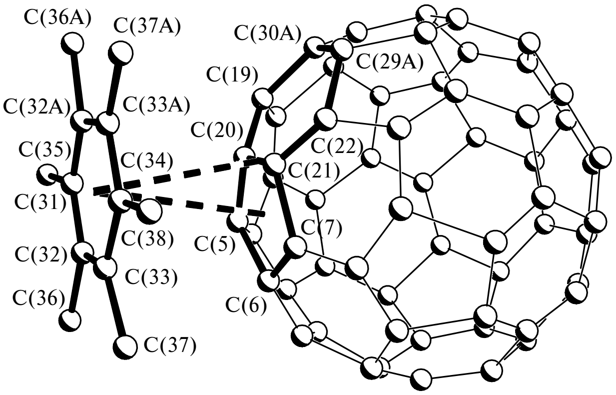

Fig. 5. Molecular structure of complex **2**.

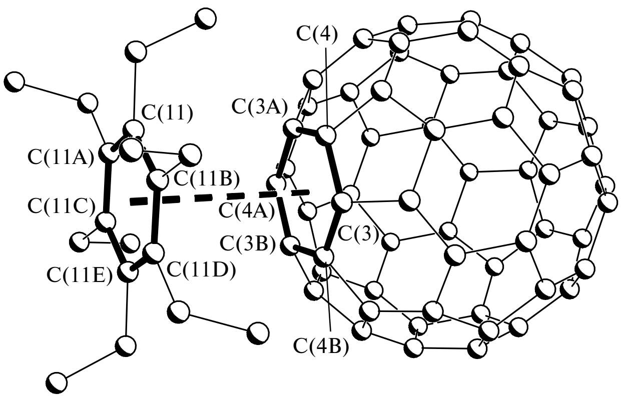

Fig. 6. Molecular structure of complex **3**.

complex **2**. Apparently, this difference is due to the greater steric volume of the Et groups compared to the Me groups. The shortest C...C distance between the Et groups and the C_{60} molecule is 3.439(2) Å, which is much smaller than the distances to the C atoms of the benzene ring (3.981(2), 3.937(2) Å).

The structures of a number of fullerene complexes with aromatic compounds (9,10-diphenylanthracene,[13] 1,3,5-triphenylbenzene,[14] biphenyl,[15] benzene,[16] and other) have now been elucidated. The shortest distances between the center of the arene in the donor molecule and the C atom, the midpoint of the C—C bond, or the center of a six-membered fullerene fragment (depending on the mutual arrangement of the donor and the acceptor) lie in the 3.180—3.486 Å range. Note that the benzene...fullerene distance in the C_{60} complex with benzene[15] (3.180 Å) is commensurable with a similar distance in molecule **2** (3.16(1) Å). Apparently, this fact is due to the predominant contribution of nonvalence contacts to the formation of the fullerene—donor molecule distance.

The results of refinement of the unit cell parameters from the powder X-ray diffraction pattern of **2** (see Fig. 2) (Rp = 8.55 and $\chi^2 = 0.81$, monoclinic cell parameters ($C2$ group): a = 12.627 Å, b = 15.764 Å, c = 10.070 Å, $\gamma = 110.426°$) are consistent with the single-crystal X-ray diffraction data, thus confirming the composition of the powder of the synthesized compound.

The DTA curve of complex **1** shows only an endothermic peak with a maximum at 533 K, which corresponds to evolution of C_6Me_6 (according to ^1H NMR spectroscopy). The thermogram of a pure C_6Me_6 sample shows an endothermic melting and sublimation peak at 443 K. Hence, C_6Me_6 is evolved from fulleride **1** during heating at a temperature exceeding the temperature of destruction of the bis(arene)chromium structure of the radical cation $(\eta^6-C_6Me_6)_2Cr^{\bullet+}$ in molecule **1** (473 K). Since the thermogram of complex **2** has an endothermic peak with a maximum at 533 K accompanied by C_6Me_6 evolution, one can suggest that the thermal decomposition of fulleride **1** involves the formation of complex **2**. The X-ray diffraction pattern of the solid residue resulting from thermal decomposition of fulleride **1** exhibits only the reflections corresponding to the cubic face-centered C_{60} phase. The solid residue is pyrophoric and easily gives off fullerene molecules on treatment with toluene. The C_{60} : Cr molar ratio is close to unity.

Thus, we accomplished the first synthesis of bis(η^6-hexamethylbenzene)chromium [60]fulleride, studied its physicochemical properties and thermal decomposition in vacuum, isolated complexes of C_{60} fullerene with C_6Me_6 and C_6Et_6, determined and compared their molecular structures, and noted the effect of nonvalence intermolecular contacts on the geometric parameters.

Experimental

The complexes were synthesized and studied in evacuated tubes in the absence of water or oxygen traces. The solvents were purified and dehydrated using standard procedures[16,17] and deaerated prior to experiments by vacuum freezing—thawing repeated three times.

Hexamethyl- and hexaethylbenzene were prepared by exhaustive alkylation of mesitylene and ethylbenzene, respectively, in the $C_6H_3Me_3$—MeI—$AlBr_3$ and C_6H_5Et—EtBr—$AlBr_3$ systems followed by five recrystallizations from hexane and two vacuum sublimations of the target products whose purity was confirmed by ^1H NMR spectroscopy and by the agreement of the measured melting points with published data.[18]

The complex $(\eta^6-C_6Me_6)_2Cr^0$ was synthesized using modification of the reported procedure[19] by the reduction of anhydrous $CrBr_3$ with Al powder in the presence of anhydrous $AlBr_3$ and C_6Me_6 at 373 K in an evacuated tube (24 h). After hydrolysis of the reaction mixture with concentrated NH_4OH, the aqueous solution of the hydroxide $(\eta^6-C_6Me_6)_2Cr^+OH^-$ was washed three times with toluene and reduced with an Al powder in an alkaline medium to $(\eta^6-C_6Me_6)_2Cr^0$ with extraction into toluene, the solvent was evaporated, and the complex was dried *in vacuo*. The individuality of the yellow-orange $(\eta^6-C_6Me_6)_2Cr^0$ complex was confirmed by ^1H NMR spectroscopy and by the melting points of the products of acid decomposition of this complex on treatment with a dilute solution of HCl (only C_6Me_6 was detected).

The ESR spectra were recorded on a Bruker ER 200D-SRC spectrometer equipped with an ER 4105 DR double resonator and an ER 4111 VT thermal controller. The IR spectra were measured on an FSM 1201 FT IR spectrometer at 293 K for suspensions in mineral and fluorinated oils or without oil (KBr pellets). The ^{1}H NMR spectra were measured on a Bruker DPX-200 instrument in $CDCl_3$.

Powder X-ray diffraction analysis was carried out on Dron 3M and URS instruments. The refinement was done using the FullProf_Suite program package.

Samples of compounds **1**, **2**, and C_6Me_6 were analyzed by DTA in evacuated ($P = 10^{-2}$ Torr) glass setups at a heating rate of 8—10 K min^{-1}. Prior to the analysis, complexes **1** and **2** were dried *in vacuo* at 373 and 293 K, respectively. The volatile products were collected in a trap cooled by liquid N_2.

The Cr content in complex **1** was calculated from the amount of Cr_2O_3 formed after the sample combustion.

Bis(η^6-hexamethylbenzene)chromium [60]fulleride $[(\eta^6\text{-}C_6Me_6)_2Cr]^{\cdot +}[C_{60}]^{\cdot -}$ (1). A solution of $(\eta^6\text{-}C_6Me_6)_2Cr^0$ in toluene was added at room temperature to a saturated toluene solution of C_{60} (0.1 g). The solvent was decanted, and the brown precipitate of compound **1** was washed three times with toluene and dried *in vacuo* (10^{-2} Torr) on a boiling water bath. Fulleride **1** is insoluble in aliphatic or aromatic solvents or THF, sparingly soluble in benzonitrile, and air sensitive. Found (%): Cr, 4.72. $C_{84}H_{36}Cr$. Calculated (%): Cr, 4.75.

The complex $C_{60} \cdot C_6Me_6$ (2). A saturated solution of hexamethylbenzene in $o\text{-}Cl_2C_6H_4$ was added to a saturated solution of fullerene (0.06 g) in $o\text{-}Cl_2C_6H_4$, and the mixture was stirred for 30 min. The solvent was decanted and the black crystalline precipitate of compound **2** was washed with hexane and dried *in vacuo* (10^{-2} Torr). Yield 80%. Powder X-ray diffraction, interplanar spacing/Å (*I* (%): 9.626 (56), 7.983 (81), 6.1236 (57), 4.8407 (100), 4.7606 (39), 4.5916 (57), 4.4125 (58), 4,0900 (42), 3.9723 (25), 3.8546 (34), 3.3015 (8), 3.2080 (26), 3.1688 (15), 3.0599 (24), 2.9926 (24), 2.9442 (23), 2.8417 (8), 2.7829 (13), 2.5871 (6), 2.5380 (11), 2.2753 (5), 2.1939 (7), 2.1309 (10), 2.0867 (6), 2.0608 (6), 2.0304 (7), 1.9741 (7), 1.8976 (6), 1.8737 (7), 1.8571 (6). IR (mineral oil), ν/cm^{-1}: 1428, 1182, 577, 526 (C_{60}); 1080 br, 796 (C_6Me_6). IR (fluorinated oil), ν/cm^{-1}: 2920, 2850, 1457, 1376 (C_6Me_6).

The complex $C_{60} \cdot C_6Et_6$ (3) can be prepared similarly to **2** but in a low yield (20%). The yield increases to 80% if solid C_6Et_6 is added to a saturated solution of fullerene in $o\text{-}Cl_2C_6H_4$ until the solution becomes colorless. The black-colored crystalline precipitate of compound **3** was washed with hexane and dried *in vacuo* (10^{-2} Torr). IR (mineral oil), ν/cm^{-1}: 1430, 1183, 577, 528 (C_{60}); 1481, 1445, 1098, 1056, 977, 826, 733, 675 (C_6Et_6).

X-Ray diffraction study. X-ray diffraction measurements for complexes **2** and **3** were carried out on a SMART Apex diffractometer (graphite monochromator, θ—ω scan mode, Mo-Kα radiation). The structures of crystals **2** and **3** were solved by the direct method and refined by least squares in the

Table 1. Selected crystal data and structure refinement parameters for complexes **2** and **3**

Parameter	**2**	**3**
Molecular formula	$C_{72}H_{18}$	$C_{78}H_{30}$
Molecular mass	882.86	967.02
Crystal size/mm	0.80×0.15×0.12	0.20×0.15×0.10
T/K	100(2)	100(2)
Space group	*C*2	*R*-3
a/Å	12.549(2)	15.7224(8)
b/Å	15.668(2)	15.7224(8)
c/Å	9.998(1)	14.239(1)
β/deg	110.455(2)	—
V/Å^3	1841.8(4)	3048.3(3)
Z	2	3
d_{calc}/g cm^{-3}	1.592	1.580
μ/mm^{-1}	0.091	0.090
Absorption corrections	By the SADABS program	
T_{min}/T_{max}	0.931/0.989	0.9822/0.9910
F(000)	900	1494
$2\theta_{max}$/deg	50	50
The number of collected reflections	7156	8153
The number of independent reflections (R_{int})	3206 (0.0344)	1201 (0.0247)
R_1 (on *F* for reflections with $I > 2\sigma(I)$)	0.1534	0.0335
wR_2 (on F^2 for all reflections)	0.3561	0.0839
The number of refined parameters	328	138
GOOF	1.061	1.062
Residual electron density peaks (min/max)/e Å^{-3}	−0.632/0.661	−0.164/0.176

anisotriopic approximation for all non-hydrogen atoms. The H atoms in structure **2** were placed into geometrically calculated positions and refined in the riding model, while those in **3** were found from the difference electron density synthesis and refined isotropically. Determination and refinement of the structures were carried out by the SHELXTL program package.[20] In complex **2**, the fullerene molecule is disordered over several positions. Since the disorder could not be eliminated, the errors in determination of the geometric characteristics and the *R*-factors for complex **2** are rather high. The errors in determination of all C—C bond lengths in molecule **2** lie in the 0.005—0.02 Å range, while for molecule **3** these values are 0.001—0.002 Å. The main crystallographic data and refinement parameters for complexes **2** and **3** are summarized in Table 1. The atom coordinates are deposited with the Cambridge Structural Database.

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