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Formation, properties, and thermal decomposition of bisarene chromium(I) and molybdenum(I) fullerides*

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Fullerides $[(\eta^6\text{-}Ph_2)_2Cr]^+[C_{60}]^{\bullet-}$, $[(\eta^6\text{-}C_{10}H_{12})_2Cr]^+[C_{60}]^{\bullet-}$ ($C_{10}H_{12}$ is tetralin), and $[(\eta^6\text{-}PhCH_3)_2Mo]^+[C_{60}]^{\bullet-}$ were synthesized. The molecular structure of $[(\eta^6\text{-}Ph_2)_2Cr]^+[C_{60}]^{\bullet-}$ was established. In this compound at 100 K, radical anions $C_{60}{}^{-\bullet}$ are linked by an ordinary bond to form dimers, whereas at 293 K they are disordered and do not form dimers. The $[(\eta^6\text{- tetralin})_2Cr]^+[C_{60}]^{\bullet-}$ fulleride is stable *in vacuo* (10^{-2} Torr) below 429 K, and $[(\eta^6\text{-toluene})_2Mo]^+[C_{60}]^{\bullet-}$ is stable below 581 K.

Key words: bisarenechromium and bisarenemolybdenum complexes, fullerene, donor-acceptor complexes, molecular structure, ESR, thermal decomposition.

Fullerene C_{60} is a relatively strong acceptor with an electron affinity of 2.67 eV, and $(\eta^6\text{-arene})_2Cr^0$ and $(\eta^6\text{-}PhCH_3)_2Mo^0$ are reducing agents; therefore, they can be used for the synthesis of new donor-acceptor complexes or salts. Bis(benzene)chromium(I), bis(toluene)chromium(I), and bis(mesitylene)chromium(I) fullerides have been synthesized and characterized.[1—4] In this work, we synthesized bis(diphenyl)chromium(I),[5,6] bis(tetralin)chromium(I), and bis(toluene)molybdenum(I) fullerides.

Results and Discussion

We found that fullerene C_{60} reacts with $(\eta^6\text{-}Ph_2)_2Cr^0$, $(\eta^6\text{-}C_{10}H_{12})_2Cr^0$, and $(\eta^6\text{-}PhCH_3)_2Mo^0$ at room temperature in toluene to form black crystalline substance **1**, brown substance **2**, and black microcrystalline substance **3**, respectively. Fullerides **1** and **2** are insoluble in aliphatic and aromatic solvents and weakly soluble in benzonitrile. Fulleride **3** is insoluble in aliphatic solvents and soluble in *N*,*N*-dimethylaniline and pyridine. The metal content in the synthesized compounds was calculated from the amounts of Cr_2O_3 and MoO_3 remained after burning. Analyses of the metal content in complexes **1**, **2**, and **3** and in the starting organometallic compounds (OMC) show that the molar ratio of OMC to fullerene in **1**, **2**, and **3** is close to 1. The IR spectra of complexes **1**, **2**, and **3** contain absorption bands characteristic of cations $(\eta^6\text{-}Ph_2)_2Cr^+$ (423, 463 cm^{-1}), $(\eta^6\text{-}C_{10}H_{12})_2Cr^+$ (400, 800 cm^{-1}), and $(\eta^6\text{-arene})_2Mo^+$ (345, 378 cm^{-1}), respectively. Absorption bands (576, 1180 cm^{-1}) in the spectra of **1**, **2**, and **3** are slightly shifted compared to those in the spectrum of C_{60}. The spectra of complexes **1** and **3** exhibit an inverse ratio of intensities of absorption bands at 525 and 576 cm^{-1} compared to that for C_{60}. At 293 K, the magnetic moments are 3.0 μ_B (**2**) and 3.1 μ_B (**3**), which values correspond to two unpaired electrons. Thus, in the compounds synthesized, the OMC molecules act as electron donors, fullerene acts as an acceptor, and complexes **1**, **2**, and **3** are salt-like fullerides of the radical-ion type.

$$(\eta^6\text{-arene})_2M^0 + C_{60} \xrightarrow{i} [(\eta^6\text{-arene})_2M]^+[C_{60}]^{\bullet-}$$

M = Mo, arene = PhMe; M = Cr, arene = Ph_2 and $C_{10}H_{12}$.

i. 293 K, 10^{-2} Torr

The ESR spectra of complex **1** in CH_2Cl_2 and complex **2** in benzonitrile represent lines with a hyperfine structure characteristic of the $(\eta^6\text{-}Ph_2)_2Cr^+$ and $(\eta^6\text{-}C_{10}H_{12})_2Cr^+$ cations (Fig. 1, *a*), $g = 1.986$, $a_H(1\ H) = 0.35$ mT, and $a_{Cr}(53\ Cr) = 1.86$ mT. The ESR spectrum of complex **3** in benzonitrile has a hyperfine structure characteristic of the $(\eta^6\text{-}PhCH_3)_2Mo^+$ cation (Fig. 1, *b*), $g = 1.985$, and $a_H(1\ H) = 0.50$ mT. The ESR spectrum of crystalline **3** at 293 K is a broad singlet with $g = 1.990$ and $\Delta H \approx 12.5$ mT (Fig. 2, *a*), a superposition of the broad and

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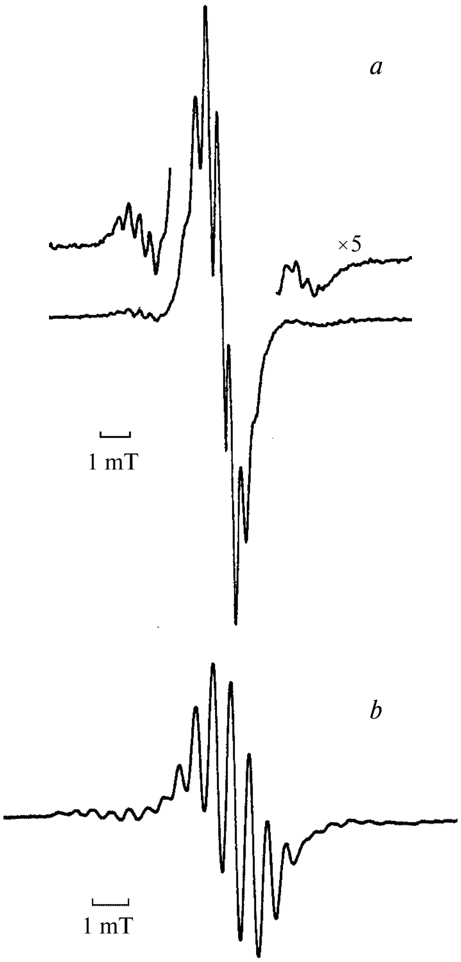

Fig. 1. ESR spectra of the $[(\eta^6\text{-}C_{10}H_{12})_2Cr]^+[C_{60}]^{\bullet-}$ (*a*) and $[(\eta^6\text{-}PhCH_3)_2Mo]^+[C_{60}]^{\bullet-}$ (*b*) complexes in benzonitrile.

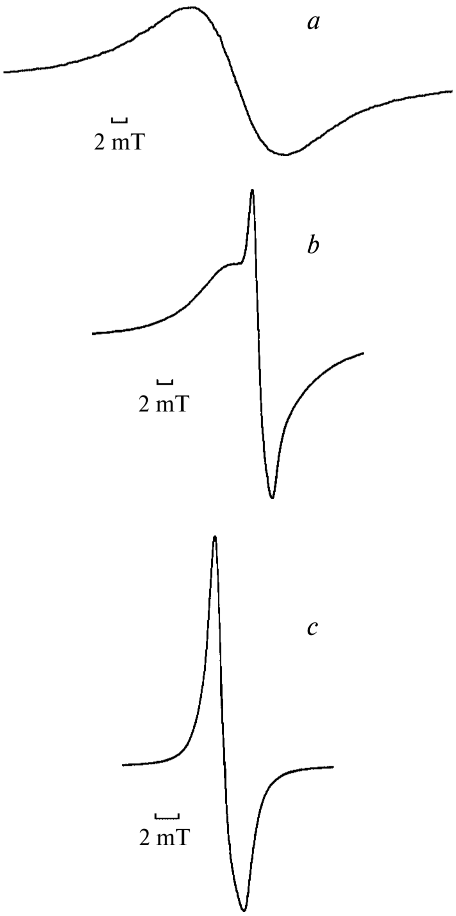

Fig. 2. ESR spectrum of the crystalline $[(\eta^6\text{-}PhCH_3)_2Mo]^+[C_{60}]^{\bullet-}$ complex at 293 (*a*), 232 (*b*), and 200 K (*c*).

narrow lines is observed in the 235—225 K interval (Fig. 2, *b*), and a narrow anisotropic line with the values characteristic of the (η^6-arene)$_2$Mo$^+$ cations ($\langle g\rangle = 1.984$ and $\langle\Delta H\rangle \approx 2.5$ mT) is observed below 225 K (Fig. 2, *c*). The ESR signal of powder **2** is a singlet with $g = 1.991$ and $\Delta H \approx 5$ mT, remaining unchanged in a temperature interval of 330—165 K. The ESR spectrum of crystalline compound **1** is a singlet with $g = 1.993$ and $\Delta H \approx 4$ mT (293 K), which changes on cooling ($g = 1.992$, $\Delta H \approx 4$ mT (77 K)) and heating ($g = 1.992$, $\Delta H \approx 4.8$ mT (376 K)).

Single crystals of **1** were obtained in an evacuated setup by the addition of a solution of (η^6-Ph$_2$)$_2$Cr^0 in toluene at room temperature to a saturated solution of fullerene in toluene until a weak yellow-brown color appeared. The X-ray diffraction study at 100 K showed that complex **1** is a centrosymmetrical dimer (Fig. 3). The C(1AA)—C(1AB) distance between adjacent fullerene molecules in molecule **1** is equal to 1.597(3) Å, which is somewhat longer than the ordinary carbon—carbon bond (1.54 Å) but much shorter than the sum of the van der Waals radii of carbon atoms (3.4 Å).[7] The C(1AA)—C(1AB) distance is close to similar distances in fullerides of (η^6-PhCH$_3$)$_2$Cr$^+$ (**4**) (1.55(5) Å)[8] and decamethylchromocene (**5**) (1.597(7) Å).[9] The bond angles at the C(1) atom in **1** range from 100.24(15)° to 116.8(8)°, indicating the sp^3-hybridization of this atom. For fullerides **4** and **5**, similar values of bond angles lie in a similar interval of 100.2(2)—113.3(2)°. The X-ray diffraction study of complex **1** at room temperature showed that the shortest C...C distance between the radical anions is ~3.2 Å. The bond angles at the carbon atoms of the shortest contact indicate their sp^2-hybridization. Thus, at room temperature $[(\eta^6\text{-}Ph_2)_2Cr]^+[C_{60}]^{\bullet-}$ is a monomer. The (η^6-Ph$_2$)$_2$Cr$^+$ cations in the structure are well ordered, and the fullerene radical anions are disordered, which prevents obtaining their exact geometric characteristics.

The differential thermal analysis of complexes **1**, **2**, and **3** was carried out in evacuated (10^{-2} Torr) glass ampules increasing temperature with a rate of 8—10 deg min^{-1}. The DTA thermogram of complex **1** contains two endotherms with maxima at 443 and 493 K,

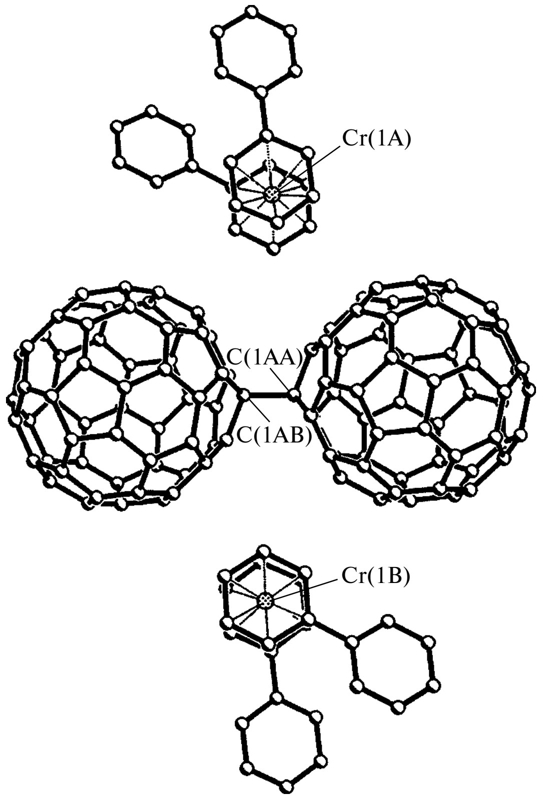

Fig. 3. Molecular structure of complex **1** (solvate molecules of toluene are not shown).

whereas the thermograms of complexes **2** and **3** exhibit endotherms in intervals of 449—563 K and 581—623 K, respectively. The thermal decomposition of complexes **1**, **2**, and **3** was studied in an evacuated setup (10^{-2} Torr). Volatiles were condensed using liquid nitrogen. Complex **1** was found to begin to decompose without melting with a noticeable rate above 423 K, while at 473 K it completely decomposes within 5 h to form diphenyl and a solid pyrophoric substance easily losing fullerene molecules when toluene is added. An analysis of the chromium content showed that the C_{60} : Cr molar ratio in this substance is close to 1. The yield of diphenyl is ~100%.

$$[(\eta^6\text{-Ph}_2)_2\text{Cr}]^+[\text{C}_{60}]^{\bullet-} \xrightarrow{i} [\text{C}_{60}\text{Cr}] + 2\ \text{Ph}_2$$

i. 423 K, 10^{-2} Torr

The C_{60} : Cr molar ratio in a solid residue remained after the thermal decomposition of complex **2** is close to 1. A solid residue of the thermal decomposition of **3** is insoluble in toluene and soluble in *ortho*-dichlorobenzene, and its C_{60} : Mo molar ratio is close to 1. According to the data of ^{1}H NMR spectroscopy, tetralin and toluene are liquid products of the thermal decomposition, and they are quantitatively isolated when complexes **2** and **3** are heated above 429 and 581 K, respectively.

$$[(\eta^6\text{-C}_{10}\text{H}_{12})_2\text{Cr}]^+[\text{C}_{60}]^{\bullet-} \xrightarrow{i} [\text{C}_{60}\text{Cr}] + 2\ \text{C}_{10}\text{H}_{12}$$

i. 429 K, 10^{-2} Torr

$$[(\eta^6\text{-PhMe})_2\text{Mo}]^+[\text{C}_{60}]^{\bullet-} \xrightarrow{i} [\text{C}_{60}\text{Mo}] + 2\ \text{PhMe}$$

i. 581 K, 10^{-2} Torr

Thus, compounds **1**, **2**, and **3** are stable in a vacuum of 10^{-2} Torr at temperatures below 423, 429, and 581 K, respectively.

Experimental

X-ray diffraction studies of complex **1** was carried out on a SMART Apex diffractometer (graphite monochromator, θ-ω scan mode, Mo-*K*α radiation). The molecular formula is $C_{91}H_{28}Cr$, the molecular weight is 1173.13, monoclinic crystal system, space group $P2(1)/c$, at 100 K a = 14.930(0), b = 25.269(2), c = 14.002(1) Å, β = 113.663(1)°, V = 4838.3(6) Å^3, Z = 4, ρ_{calc} = 1.611 g cm^{-13}, F_{000} = 2392, μ = 0.301 mm^{-1}, 1.61° < θ < 26.00°. The total number of collected reflections was 28667, among which 9489 reflections were independent [R_{int} = 0.0536], GOOF = 1.039, R = 0.0541, wR^2 = 0.1542, residual electron density 0.916/—0.561 e•A^{-3}.

The structure was solved by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were placed in geometrically calculated positions and refined isotropically in the riding model. A solvate toluene molecule was revealed in the structure of crystal **1**. The data were collected and processed and unit cell parameters were refined using the SMART[10] and SAINT Plus[11] programs. All calculations on determination and refinement of the structure were performed by the SHELXTL programs.[12]

ESR spectra were recorded on a Bruker ER 200D-SRC spectrometer equipped with an ER 4105DR resonator (operating at 9.5 GHz) and an ER 4111VT temperature-controlled unit. The values of *g* factor were measured using diphenylpicrylhydrazyl as standard.

Reaction products were synthesized and isolated in an evacuated (10^{-2} Torr) all-sealed setup. Solvents were deaerated before use by triple freezing, evacuation (10^{-2} Torr), and thawing out.

Synthesis of bis(η^6-diphenyl)chromium(I) [60]fulleride [$(\eta^6$-Ph$_2)_2$Cr]$^+$[C$_{60}$]$^{\bullet-}$ (1). A solution of $[(\eta^6\text{-Ph}_2)_2\text{Cr}]^0$ in toluene was added to a saturated solution of C_{60} in toluene at room temperature. The solvent was decanted, and a black crystalline precipitate of **1** was washed three times with toluene and dried at 10^{-2} Torr in a boiling water bath. Found (%): Cr, 4.81. $C_{84}H_{20}Cr$. Calculated (%): Cr, 4.81.

Synthesis of bis(η^6-1,2,3,4-tetrahydronaphthalene)chromium(I) [60]fulleride [$(\eta^6$-C$_{10}$H$_{12})_2$Cr]$^+$[C$_{60}$]$^{\bullet-}$ (2) was synthesized similarly to compound **1**. Found (%): Cr, 5.00. $C_{80}H_{24}Cr$. Calculated (%): Cr, 5.02.

Bis(η^6-toluene)molybdenum(I) [60]fulleride [$(\eta^6$-PhCH$_3)_2$Mo]$^+$[C$_{60}$]$^{\bullet-}$ (3). An excess of a concentrated solution of $(\eta^6\text{-PhCH}_3)_2\text{Mo}^0$ in toluene was added to a saturated solution of C_{60} in toluene at room temperature. The solvent was decanted, and a black microcrystalline precipitate **3** was washed three times with toluene and dried at 10^{-2} Torr and 403 K. Found (%): Mo, 9.62. $C_{74}H_{16}Mo$. Calculated (%): Mo, 9.60.

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