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Synthesis, Structure, and Thermolysis of (Fullerene)(toluene)dicarbonylchromium

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(Fullerene)(toluene)dicarbonylchromium (η^6-$C_6H_5CH_3$)Cr(CO)$_2$(η^2-C_{60}) has been synthesized and characterized by ^{1}H NMR, IR, and UV spectroscopy. Its molecular structure has been determined and studied. Heating (fullerene)(toluene)dicarbonylchromium in vacuum at temperatures above 383 K leads to the destruction of the (toluene)dicarbonylchromium moiety.

Fullerene C_{60} has 30 essentially localized double bonds and can form η^2 complexes with transition metals. Molybdenum and tungsten π complexes of dihapto-coordinated fullerene with different ligands, such as CO, phenanthroline, α,α-dipyridyl, triphenylphosphine, and maleic and fumaric acid esters, have been prepared and structurally characterized [1–4]. The η^2-C_{60} complex with the (diphosphine)tricarbonylchromium moiety has been characterized by spectral methods [5]. As is known, (arene)tricarbonylchromium complexes can exchange the CO group for alkenes when exposed to UV irradiation [6]. Therefore, we studied the interaction of C_{60} with (toluene)tricarbonylchromium under UV irradiation.

We found that (toluene)tricarbonylchromium reacts with fullerene in a toluene solution when exposed to light with a wavelength shorter than 400 nm at room temperature. The reaction yields a green compound (**1**), which is soluble in aromatic solvents; poorly soluble in CH_2Cl_2, $CHCl_3$, and THF; insoluble in aliphatic solvents; and stable in air in the dark and in a vacuum of 10^{-2} torr below 383 K. In the IR spectrum of **1**, the C–O (1941 cm^{-1}), C–H (809 cm^{-1}), and Cr–CO (657 cm^{-1}) vibration bands are bathochromically shifted as compared to the initial (toluene)tricarbonylchromium; the other bands (485, 629, 1031, 1419, and 1886 cm^{-1}) do not change their position. As compared to the initial C_{60}, in the IR spectrum of **1**, the $T_u(2)$ band at 581 cm^{-1} is hypsochromically shifted and its intensity is equal to the intensity of the $T_u(1)$ band at 524 cm^{-1}; in addition, a new band is observed at 563 cm^{-1}. These changes can be evidence of deformation of C_{60} incorporated in **1**. According to chemical analysis data, the molar ratio C_{60} : Cr is close to 1. The electronic absorption spectrum of **1** in a CH_2Cl_2 solution (Fig. 1) shows bands typical of the initial C_{60} (257, 329, and 602 nm) and two new bands (448 nm, which is typical of fullerene addition products, and 650 nm); at the same

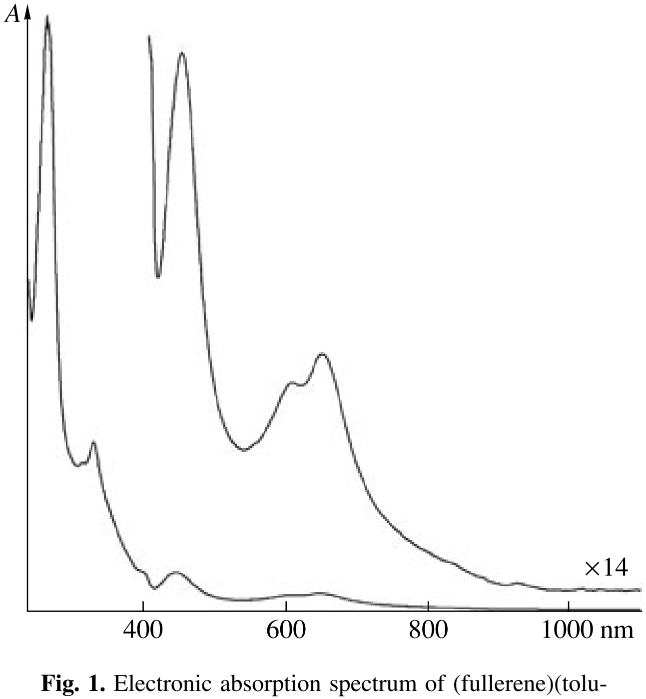

Fig. 1. Electronic absorption spectrum of (fullerene)(toluene)dicarbonylchromium in CH_2Cl_2.

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time, the C_{60} absorption maximum at 540 nm in the visible region is absent. On heating in a vacuum of 10^{-2} torr, **1** begins to decompose above 383 K with evolution of gaseous products. According to ^1H NMR, the liquid decomposition product is toluene, which is completely removed above 523 K. X-ray powder diffraction shows that the solid residue contains the hexagonal phase of C_{60}, has a molar ratio C_{60} : Cr close to 1, and readily loses C_{60} when treated with toluene. The amount of the evolved toluene is consistent with the Cr content in complex **1**.

X-ray crystallography demonstrates that complex **1** consists of a C_{60} molecule, a toluene molecule, two CO molecules, and a Cr atom (Fig. 2). The major geometric characteristics of the $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2$ moiety in complex **1** are close to the analogous parameters of the $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$ molecule [7]. Hence, the bonds formed by the Cr atom with toluene and the two CO molecules in **1** are similar to those in $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$. The shortest distance between the toluene and fullerene molecules C(66)–C(3) (3.073 Å) is noticeably smaller than the sum of the van der Waals radii of the carbon atoms and smaller than the analogous distance in the complex of C_{60} with benzene (3.180 Å) [8]. We may assume that the Cr atom interacts with the C(1)–C(2) bond of C_{60} since it sits atop the midpoint of this bond (Fig. 2). The distances between the Cr(1) atom and the midpoint of the C(1)–C(2) bond is 2.079(3) Å. A similar situation is observed in methyl acrylate complexes of (hexamethylbenzene)dicarbonylchromium (**2**) and (*o*-xylene)dicarbonylchromium (**3**) [9], where the chromium atom interacts with the double bond of the acrylate. In these complexes, the Cr atom is located above the midpoint of the double bond. The distances between the Cr atom and the midpoint of the C=C bond in **2** and **3** are, respectively, 2.097 and 2.068 Å, which is comparable with the analogous distance in **1**. The Cr(1)–C(1,2) distances are 2.203(3) and 2.202(3) Å, which is somewhat shorter than the distances between the Cr atom and the toluene molecule (2.210(3)–2.261(3) Å). The analogous Cr–C(C=C) distances in complexes **2** and **3** fall within the range 2.178–2.214 Å. The C(1) and C(2) atoms form a 6-6 bond in fullerene. Its length (1.457(4) Å) exceeds the lengths of the other 6-6 bonds of the fullerene moiety (1.374(4)–1.404(5) Å). The lengths of the 6-5 bonds in C_{60} involving the C(1) and C(2) atoms fall within the range 1.472(4)–1.495(4) Å and are considerably longer than the other 6-5 bonds of C_{60} (1.432(4)–1.465(4) Å). It is worth noting that the bond angles at the C(1) and C(2) atoms belonging to the pentagons, C(6)C(1)C(9) (104.6(2)°) and C(12)C(2)C(3) (104.6(2)°), are considerably smaller than the analogous angles at the other carbon atoms of C_{60} (107.4(3)°–123.1(3)°). In addition, the deviation from the coplanar arrangement of the six-membered fullerene rings C(1–6) and C(1,2,9–12), which share the C(1)–C(2) edge, is 5.4° and 6.0°, respectively, whereas the other fullerene hexagons are planar within 1°. This points to a significant interaction of Cr with C_{60}; as a result, the C(1) and C(2) atoms are shifted with respect to the spherical C_{60} toward the Cr atom. Thus, C_{60} forms a bond to the Cr atom in **1** as olefins do in (arene)(olefin)dicarbonylchromium complexes. Compound **1** is a π complex of fullerene: $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2(\eta^2\text{-}C_{60})$.

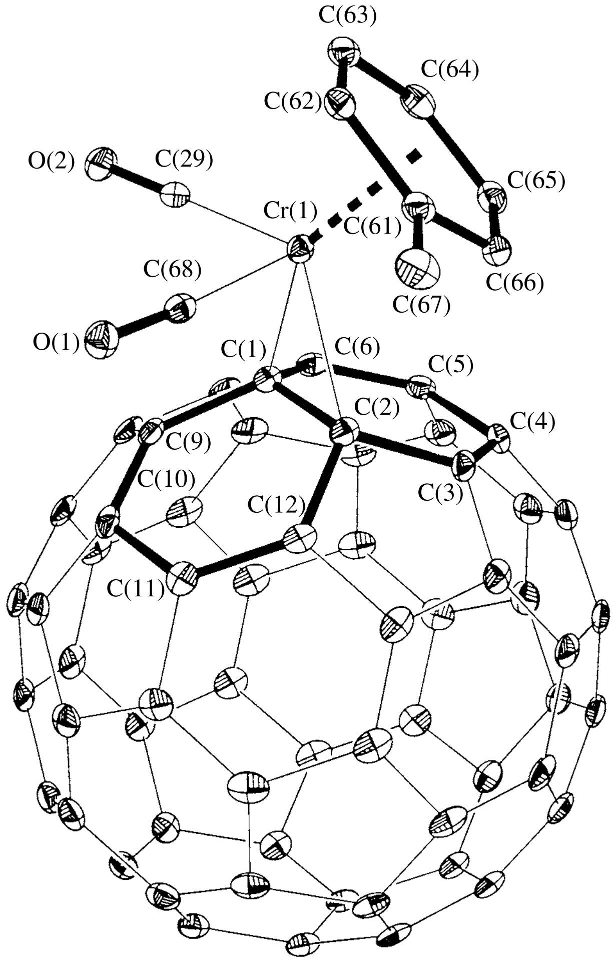

Fig. 2. Molecular structure of (fullerene)(toluene)dicarbonylchromium at 100 K.

$$C_{60} + (\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$$

$$\xrightarrow[293\text{ K, 7 h}]{350\text{–}400\text{ nm, toluene}} (\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2(\eta^2\text{-}C_{60}) + CO.$$

In the ^1H NMR spectrum of **1**, the protons signal of toluene bonded to the Cr atom (6.070, 6.040, 6.008, 5.932, 5.900, 5.869, 5.788, 5.758, and 2.617 ppm) are shifted downfield as compared to the signals of the initial complex $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$ (5.438, 5.406, 5.374, 5.162, 5.132, 5.100, and 2.188 ppm). This can be evidence that the electron-accepting effect of the

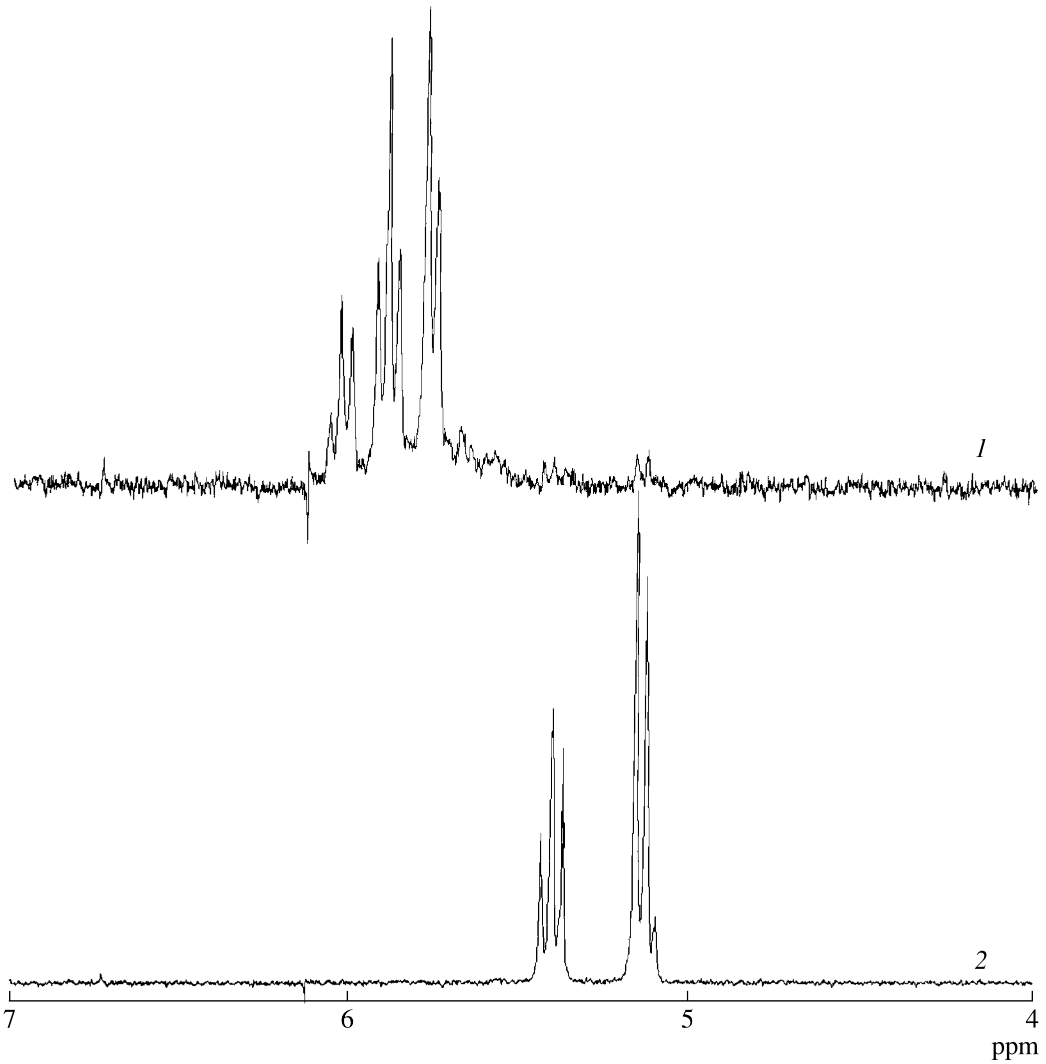

Fig. 3. ^{1}H NMR spectra of (*1*) $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2(\eta^2\text{-}C_{60})$ and (*2*) $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$.

$Cr(CO)_2(\eta^2\text{-}C_{60})$ group on toluene is stronger than that of the $Cr(CO)_3$ group in $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$.

EXPERIMENTAL

Complex **1** was synthesized in evacuated ampoules under oxygen- and moisture-free conditions. The solvents were dried by common procedures [10]. Toluene was degassed by means of three freezing–thawing cycles in vacuum.

IR spectra were recorded as Nujol mulls on an FSM 1201 IR FT spectrophotometer at 293 K. ^{1}H NMR spectra were recorded as solutions in $CDCl_3$ on a Bruker DPX-200 spectrometer. Chemical shifts were referenced to tetramethylsilane. Electronic absorption spectra were recorded on a Perkin Elmer Lambda 25 spectrophotometer. Thermolysis was carried out in evacuated glassware. Liquid products were condensed in a trap cooled with liquid nitrogen. The Cr content of complex **1** and of the products of its thermal destruction was calculated from the weight of Cr_2O_3 after burning the samples.

(Fullerene)(toluene)dicarbonylchromium $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2(\eta^6\text{-}C_{60})$. A solution of 0.171 g of C_{60} (23.75 mmol) and 0.0573 g of $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$ (25.13 mmol) in 100 mL of toluene was placed in a molybdenum glass ampoule and irradiated, with stirring, by sunlight for 7 h or with a low-pressure mercury lamp for 3 h. The reaction mixture was filtered and chromatographed on silica gel (elution with toluene–hexane (1 : 1)), collecting the green fraction. The reaction product in air was carefully protected from light. The solvent was removed in vacuum. The residue was washed with hexane (5 × 15 mL) and dried in a vacuum of 10^{-2} torr at 353 K. The yield of dark green microcrystals of $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2(\eta^2\text{-}C_{60})$ was 27% in terms of C_{60}.

For $C_{69}H_8O_2Cr$ anal. calcd. (wt %): Cr, 5.65.

Found (wt %): Cr, 5.59.

Single crystals of **1** were obtained by diffusion of hexane into a chlorobenzene solution (15 mL) containing **1** (20 mg) and cobalt(II) octaethylporphyrin (18 mg). The components were dissolved in the dark without heating, the solution was filtered, and hexane (25 mL) was added.

X-ray crystallography data on **1** were collected on a SMART Apex diffractometer (graphite monochromator, ω–φ scan mode, MoK_α radiation). The crystals of **1** ($0.92 \times 0.29 \times 0.03$ mm) are monoclinic at 100 K: a = 10.1001(10) Å, b = 22.992(2) Å, c = 16.7351(17) Å, β = 91.224(2) Å, space group $P2(1)/n$, V = 3885.3(7) Å^3, Z = 4, ρ_{calcd} = 1.766 g/cm^3, F_{000} = 2080, μ = 0.432 mm^{-1}, $1.77° < \theta < 29.15°$. A total of 40 486 reflections were collected, 10 374 of them being unique (R_{int} = 0.0792); GOF = 1.027, R = 0.0643 and $wR2$ = 0.1535 [$I > 2\sigma(I)$], R = 0.1100 and $wR2$ = 0.1768 (for all reflections); residual electron density, 1.035/–0.696 e Å^{-3}.

The structure was solved by direct methods and refined by least-squares calculations in the anisotropic approximation for non-hydrogen atoms. The H atoms were placed in geometrically calculated positions and refined isotropically as riding on their parent atoms. The crystal structure of **1** contains chlorobenzene molecules of solvation in the ratio **1** : C_6H_5Cl = 1 : 1. All calculations were performed with the SHELXTL program package [11].

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