Organometallic Chemistry

Synthesis, crystal structure, and spectral studies of the molecular complex of [60]fullerene with chloro(triphenylphosphine)gold(I), $C_{60} \cdot 2[(Ph_3P)AuCl]$

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The molecular complex $C_{60} \cdot 2[(Ph_3P)AuCl]$ (**I**) was synthesized. The crystal and molecular structure of **I** was established by X-ray diffraction analysis. At room temperature, the [60]fullerene molecules in complex **I** are ordered due to $\pi-\pi$ interactions between C_{60} and the phenyl rings of the chloro(triphenylphosphine)gold(I) molecules. The satellite structure, which accompanies the C1s photoelectron peak of complex **I**, is indicative of a partial suppression of a channel of losses due to $\pi \rightarrow \pi^*$ transition in the phenyl ring. The IR spectral data indicate that either a charge is absent or the charge transfer to the fullerene molecule is negligible.

Key words: chloro(triphenylphosphine)gold(I), molecular complex, [60]fullerene, X-ray diffraction analysis, crystal structure, XPS and IR spectroscopy, intermolecular interactions.

A complex was obtained in the $C_{60}-Ph_3PAuCl$ system.[1–3] The available data on the composition and structure of this complex are contradictory.

In the present work, we report data on the synthesis, spectral studies, and crystal structure of $C_{60} \cdot 2[(Ph_3P)AuCl]$.

Experimental

Synthesis of the [60]fullerene complex with chloro(triphenylphosphine)gold(I). A hot solution of pure C_{60} (99.9% according to HPLC; 7.2 mg, 0.01 mmol) in freshly distilled benzene (20 mL) and a hot solution of an equimolar amount of $(Ph_3P)AuCl$ (Aldrich) in benzene (20 mL) were mixed at 50 °C, kept at this temperature for 30 min, and then cooled to room temperature. After two weeks, lustrous black crystals formed at the bottom of the flask as a result of slow evaporation of the solution to 2–3 mL. The crystals were filtered off, washed with benzene and ether, and dried *in vacuo*. Found (%): C, 67.18; H, 1.72; Cl, 4.21. $C_{96}H_{30}Au_2Cl_2P_2$. Calculated (%): C, 67.37; H, 1.76; Cl, 4.15. The elemental composition agrees with the X-ray diffraction data.

X-ray diffraction study was performed on an automated four-circle Kuma Diffraction diffractometer ($\omega/2\theta$ scanning technique, scan width $\omega = 0.60 + 0.35\tan\theta$, scan rate about 3.1–6.6 deg min^{-1}, (Cu-Kα) radiation, graphite monochromator). A total of 3174 reflections were collected, of which 2104 reflections were used in the structure refinement; $(2\theta)_{max} = 160.22°$; the range of measured indices h,k,l: $-15 \le h \le 13$, $0 \le k \le 15$, $0 \le l \le 40$. The absorption correction was applied using the Difabs program.[4] The X-ray diffraction data were collected at room temperature.

Complex **I** was crystallized as dark-red oval platelets. The principal crystallographic data for $C_{60} \cdot 2[(Ph_3P)AuCl]$, $C_{96}H_{30}Au_2Cl_2P_2$: $M = 1709.97$, trigonal system, $a = b = 12.006(5)$ Å, $c = 35.50(1)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 4427(3)$ Å^3 (the parameters were refined by the least-squares method using 25 automatically centered strong reflections, $\lambda =$

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1.54175 Å), space group $P\bar{3}$, $Z = 3$, $d_{calc} = 1.924$ g cm^{-3}, $F(000) = 2484$. The dimensions of the crystal were 0.36×0.20×0.07 mm; μ(Cu-Kα) = 11.025 mm^{-1}. The quality of the experimental data was monitored by checking two standard reflections whose intensities were measured after each 50 reflections. These two standard reflections remained unchanged throughout data collection.

The IR spectra were measured on a Perkin—Elmer 1725 X IR Fourier spectrometer in KBr pellets.

The X-ray photoelectron spectra were excited with (Al-Kα) radiation ($h\nu$ = 1486.6 eV). Procedures for the preparation of samples and details of the experimental apparatus have been described previously.[5]

X-ray diffraction analysis and refinement. The crystal structure of **1** was solved by the direct method followed by calculations of Fourier syntheses using the SHELX-86[6] and SHELXL-93 program packages.[7]

The structure was refined by the least-squares method with anisotropic thermal parameters for Au, Cl, and P atoms and with isotropic thermal parameters for C atoms based on all measured reflections with the use of the SHELXL-93 program package. The final value of the R factor was 0.078 for 1760 reflections with $I > 2\sigma(I)$.

Based on systematic absence conditions, the symmetry of the structure may be assigned to one of five R-centered trigonal space groups ($R\bar{3}$, $R3$, $R3m$ $R32$, or $R\bar{3}m$). However, the structure solution in all groups gave invalid structural motifs. In all cases, short C—C contacts between the adjacent $(Ph_3P)AuCl$ molecules (C—C ~1.7 Å) appeared, which indicate that the space group is in error, the positions of the C atoms of fullerene being correctly described in all these groups. Therefore, the R unit cell for **1** is pseudosymmetrical. The only correct structural motif in which shortened contacts are absent was found in the low-symmetry space group $P\bar{3}$ and the structure was solved in this group. Due to the presence of the pseudosymmetry in complex **1**, the X-ray diffraction data were inadequate to perform the complete structure refinement. As a result, the bond lengths and bond angles in the C_{60} and $(Ph_3P)AuCl$ molecules cannot be analyzed in detail. The determined structure was tested using the Platon program[7] and it was demonstrated that the positions of the fullerene and $(Ph_3P)AuCl$ molecules can be described in the $R\bar{3}m$ and $P\bar{3}$ space groups, respectively. In both groups, the above-described short C—C contacts appear, which is highly improbable and is in contradiction with the data of IR and X-ray photoelectron spectroscopy. All calculations were carried out on a Pentium-100 PC using the WinGX program package.[8]

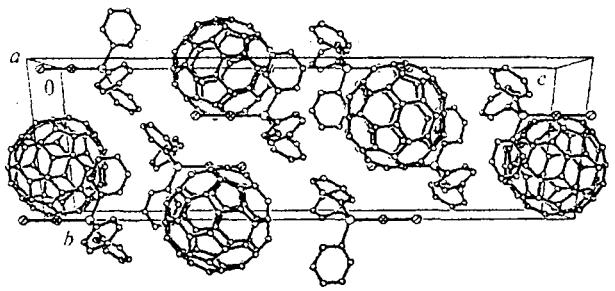

Fig. 1. Fragment of the crystal structure of the $C_{60} \cdot 2[(Ph_3P)AuCl]$ complex.

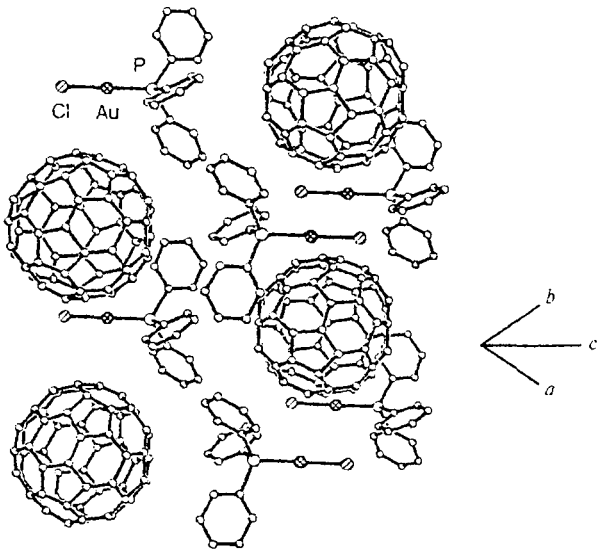

Fig. 2. Alternation of the fullerene and $(Ph_3P)AuCl$ molecules along the a axis of the crystal.

The atomic coordinates, the bond lengths, and the bond angles in the structure of $C_{60} \cdot 2[(Ph_3P)AuCl]$ were deposited with the Cambridge Structural Database.

Results and Discussion

The crystal structure of complex **1** (Fig. 1) consists of three independent C_{60} molecules and six $(Ph_3P)AuCl$ molecules. The threefold rotation axis passes through

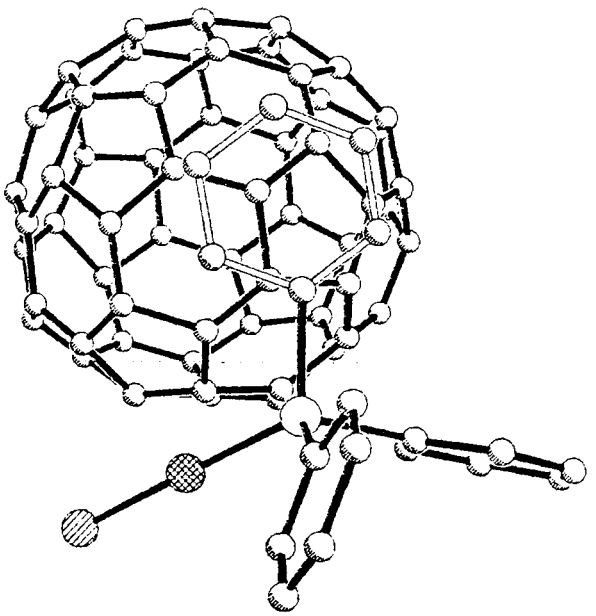

Fig. 3. Projection of the C_{60} molecule onto the plane of the phenyl ring of the $(Ph_3P)AuCl$ molecule in complex **1** (the bonds in the phenyl ring are not hatched).

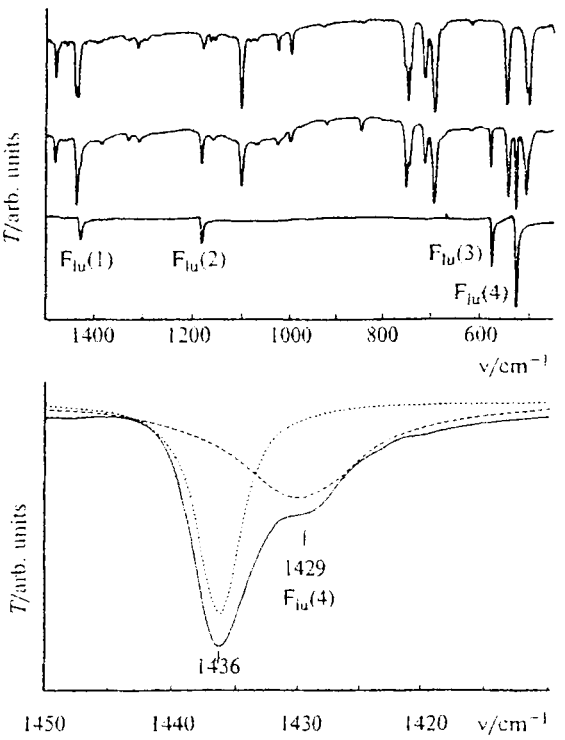

Fig. 4. *a*, IR spectra of C_{60} (*1*), $C_{60} \cdot 2[(Ph_3P)AuCl]$ (*2*), and $(Ph_3P)AuCl$ (*3*) (KBr pellets, ~20 °C); *b*, deconvolution of the overall absorption band at 1436 cm^{-1}.

the centers of the C_{60} molecules and through the Au, Cl, and P atoms. The C_{60} and $(Ph_3P)AuCl$ fragments alternate along the *a* axis of the crystal (Fig. 2). The fullerene molecules are surrounded on four sides by the phenyl rings of the $(Ph_3P)AuCl$ molecules.

Symmetry of the fullerene and $(Ph_3P)AuCl—C_3$ molecules. The Cl—Au—P fragment of the $(Ph_3P)AuCl$ molecule is linear. The Au—Cl and Au—P distances are in the ranges of 2.24—2.32 and 2.21—2.27 Å, respectively. The Au—P—C and C—P—C bond angles are in the ranges of 111.91—116.09° and 102.12—105.15°, respectively.

The C_{60} molecules in complex **1** are ordered due to interactions between the π-systems of the phenyl rings of the $(Ph_3P)AuCl$ molecules and C_{60}. These interactions are realized primarily through the double bonds of the fullerene molecules. Each phenyl fragment of the $(Ph_3P)AuCl$ molecule is directed toward one of the three adjacent C_{60} molecules so that the center of the phenyl fragment is located above the bonds between the five- and six-membered rings of the fullerene molecule (Fig. 3), as has been observed previously in the $(Ph_4P)_2C_{60}Hal$ (Hal = Br or I)[9] and $(Ph_4As)_2C_{60}Cl$ salts[9] and in the $C_{60} \cdot 6SbPh_3$ molecular complex.[10] This fact indicates that the electron density is nonuniformly distributed both in the neutral and charged fullerene species, the maxima corresponding to the bonds between the six- and five-membered rings.

Below are given the distances (d/Å) from the planes of the phenyl rings of the donor molecules in air-stable fullerides $(Ph_4P)_2C_{60}Hal$ (Hal = Br or I) and in the molecular complex $C_{60} \cdot 2[(Ph_3P)AuCl]$ to the atoms of the C_{60} molecule nearest to the planes of the phenyl rings (d_1) (d_2 is the distance between the centers of the fullerene molecules and d_3 is the distance between the phosphorus atom and the C_{60} molecule):

Compound	d_1	d_2	d_3
$C_{60} \cdot 2[(Ph_3P)AuCl]$ (**1**)	3.31	12.000	5.349
$(Ph_4P)_2C_{60}I$ (**2**)	3.65	12.495	4.683
$(Ph_4P)_2C_{60}Br$ (**3**)	3.66	12.559	4.590

It can be seen that the phenyl rings of the $(Ph_3P)AuCl$ molecules in complex **1** are located closer to the fullerene molecules than the phenyl rings of the $(Ph_4P)^{+1}$ cations in salts **2** and **3**. The P atoms in **1** are at longer distances from the C_{60} molecules than the analogous atoms in salts **2** and **3**.

Polarization van der Waals forces play an important role in [60]fullerene complexes due to the high polarizability of [60]fullerene (~85 Å^3).[11] Electrostatic interactions are primarily determined by the dispersion component, whose energy depends on the distance between the donor and the acceptor. To enhance these interactions, the donor molecule should approach the spherical fullerene molecule as close as possible, which can be realized only through geometric distortion of the donor molecule. In the case of formation of a charge transfer complex of fullerene with donor molecules, the expenditure of energy for decreasing the delocalization in the electron system of the donor molecule is compensated by the gain in energy due to efficient dispersion interactions between both components of the complex. In this case, the donor molecule adopts a new conformation, which allows this molecule to approach the fullerene molecule most closely.

It is known that force constants of bonds depend on the electron density on the molecule. Hence, as has been demonstrated previously,[12,13] the degree of charge transfer to the fullerene molecule can be determined by IR spectroscopy because the charge transfer is manifested as a linear frequency shift of at least the fundamental vibrational mode of C_{60} (1429 cm^{-1}).

The IR spectrum of the compound under study (Fig. 4) has all absorption bands caused by vibrations of the atoms of the high-symmetry (I_h) C_{60} molecule and the triphenylphosphine fragment of the $(Ph_3P)AuCl$ salt. A number of bands in the spectrum of the complex are shifted relative to their positions in the spectra of the "pure" acceptor and donor molecules. The position of the $F_{1u}(4)$ absorption band is shown in Fig. 4, *a*. In the spectrum of the complex under study, this band is superimposed on the absorption band caused by vibrations of the atoms of the triphenylphosphine fragment.

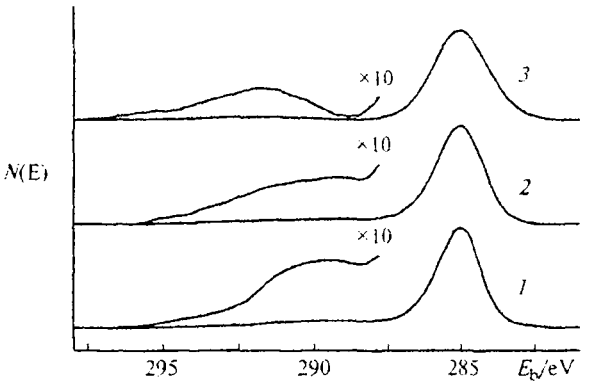

Fig. 5. X-ray photoelectron C1s spectra of C_{60} (*1*), $(Ph_3P)AuCl$ (*2*), and $C_{60} \cdot 2[(Ph_3P)AuCl]$ (*3*) after subtraction of the linear background and normalization of the total intensity.

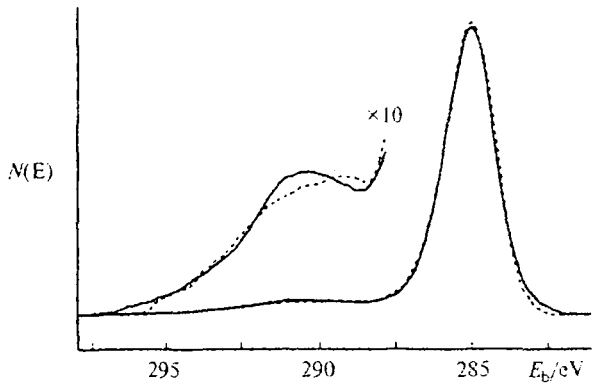

Fig. 6. Superposition of the C1s spectra of $(Ph_3P)AuCl$ and C_{60} in a ratio of 3 : 5 (solid line) and the experimental C1s spectrum of $C_{60} \cdot 2[(Ph_3P)AuCl]$ (dashed line).

The resolution of the overall absorption band into components demonstrated that the position of the component, which we identified as the $F_{1u}(4)$ mode, has no negative shift relative to that in pure C_{60}. Below are given the positions of the $F_{1u}(4)$ mode in the compound under study and in the reference compounds. The shift of this band correlates with the charge on the fullerene molecule[14]:

Compound	ν_1/cm^{-1}	Compound	ν_1/cm^{-1}
$[Ph_4As]_2C_{60}Cl$[13]	1390	RbC_{60}[12,14]	1398
$[Ph_4P]_2C_{60}Cl$[13]	1394	$C_{60} \cdot 2[(Ph_3P)AuCl]$	1429
$[Ph_4P]_2C_{60}I$[13]	1394	C_{60}[15]	1429
$[Ph_4P]_2C_{60}Br$[13]	1394		

Consequently, the charge transfer between the donor and the fullerene molecule in the compound under study is absent (or is insignificant).

A comparison of separate groups of absorption bands, which are determined by vibrations of the atoms of the donor molecule (for example, at 506 or 750 cm^{-1}), demonstrated that the conformations of these groups in the complex under study and in pure $(Ph_3P)AuCl$ are somewhat different. In the spectrum of the $C_{60} \cdot 2[(Ph_3P)AuCl]$ complex, no new absorption bands are observed compared to the spectra of the initial compounds. This indicates that the compound under study does not contain polymeric chains of the donor molecules linked through the phenyl rings. The possibility of formation of these chains in the $C_{60} \cdot 2[(Ph_3P)AuCl]$ compound of similar composition has been mentioned previously.[3]

The X-ray photoelectron spectra of the crystals of $C_{60} \cdot 2[(Ph_3P)AuCl]$ are virtually identical to those of the $C_{60} \cdot 2Ph_3PAuCl \cdot 0.1C_6H_5Me$ compound studied previously.[4] The crystals are stable under conditions of measurements of X-ray photoelectron spectra (vacuum, X-ray radiation). The composition of near-the-surface layers of the crystals is close to the composition by volume. In the compound under study, a channel of losses determined by $\pi \rightarrow \pi^*$ transitions in the phenyl ring typical of many triphenylphosphine derivatives is suppressed.

The X-ray photoelectron C1s spectra of solid fullerene, the crystals under study, and the $(Ph_3P)AuCl$ salt are shown in Fig. 5. The spectrum of $(Ph_3P)AuCl$ has a pronounced satellite (at 292 eV) located in the vicinity of the photoelectron peak on the side of higher energies. This satellite is caused by excitation of transitions in the phenyl rings and is typical of other gold complexes with triphenylphosphine.[16] In the case of solid C_{60}, the satellite is located closer to the photoelectron peak and it is of different nature, *viz.*, this satellite appears as a result of a loss in excitation of plasma oscillations of valence electrons (see, for example, Ref. 17). Based on the different nature of the satellites and the absence of charge transfer between the donor and fullerene molecules, it can be suggested that the satellite structure in the vicinity of the photoelectron peak of the compound under study is determined by a simple superposition of the spectra of $(Ph_3P)AuCl$ and C_{60} with the corresponding weights. This superposition was constructed (Fig. 6). However, it differs substantially from the experimental pattern primarily by the high intensity in proximity to 292 eV. We attributed the decrease in the intensity of the $\pi \rightarrow \pi^*$ transition to shortened contacts between the fullerene molecule and the phenyl rings of $(Ph_3P)AuCl$ in the crystal under study as well as to the strong polarizability of fullerenes. Previously, this effect has been observed[18] in the $[Ph_4Y]_2[C_{60}][X]$ compounds (Y = P or As; X = Cl, Br, or I).

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