

# PALLADIUM COMPLEXES WITH FULLERENE C<sub>60</sub>: X-RAY PHOTOELECTRON SPECTROSCOPY AND MAGNETOCHEMISTRY

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## Introduction

We present the results of a study palladium fulleride C<sub>60</sub>Pd<sub>n</sub> with n=1-4.9 and complex (η<sup>2</sup>-C<sub>60</sub>)Pd(PPh<sub>3</sub>)<sub>2</sub> by the methods of X-ray photoelectron spectroscopy (XPS), which makes it possible to obtain information on the electronic structure of the compound under study, and magnetochemistry.

## Experimental

Complex (η<sup>2</sup>-C<sub>60</sub>)Pd(PPh<sub>3</sub>)<sub>2</sub> and C<sub>60</sub>Pd<sub>n</sub> was synthesized as described in [1,2]. Chemical analysis of three samples demonstrated that the composition of palladium fulleride conformed to the formula C<sub>60</sub>Pd<sub>n</sub>, where n= 1.0, 2.9, and 4.9, respectively.

XPS were excited by MgKα radiation (hν = 1253.6 eV). The power drawn by the X-ray tube did not exceed 240 W. The spectra were calibrated by the C1s peak (285.0 eV) from C atoms of fullerene. Sample preparation for XPS was described in [3]. Magnetic susceptibility was measured by using the Faraday balance.

## Results and Discussion

Position of the analytical peaks in XPS of the complex (η<sup>2</sup>-C<sub>60</sub>)Pd(PPh<sub>3</sub>)<sub>2</sub> under study are presented in Table. The formal substitution of two PPh<sub>3</sub> groups for two Cl<sup>-</sup> ions in Pd(PPh<sub>3</sub>)<sub>4</sub> leads to the shift Pd3d<sub>5/2</sub> peak by 2.3 eV, but the substitution of these two groups for one η<sup>2</sup>-C<sub>60</sub> ligand shifts the Pd3d<sub>5/2</sub> peak only by 0.9 eV. Hence in accordance with the correlation between E<sub>b</sub>(Pd3d<sub>5/2</sub>) and Pd oxidation number for a series Pd compounds we can attributed to Pd atoms in the complex the formal charge +1.

To test the reality of this assumption we measured the magnetic susceptibility for the complex (χ<sub>M</sub>, 10<sup>5</sup> CGS units per mole). It was really shown that at the temperatures higher than 180K the susceptibility remains practically unchanged and its value is equal to 650 ± 35. At lower temperatures the χ<sub>M</sub>(meas) is slightly increased.

Consideration of the diamagnetic correction in the case of η<sup>2</sup>-C<sub>60</sub> ligand seems to be ambiguous. On one hand,

Table. Position of the Pd3d<sub>5/2</sub> X-ray photoelectron peak (in eV) of (η<sup>2</sup>-C<sub>60</sub>)Pd(PPh<sub>3</sub>)<sub>2</sub> complex and C<sub>60</sub>Pd<sub>n</sub> compounds.

	Complex	Pd 3d <sub>5/2</sub>
1.	(η <sup>2</sup> -C <sub>60</sub> )Pd(PPh <sub>3</sub> ) <sub>2</sub>	336.6
2.	Pd(PPh <sub>3</sub> ) <sub>4</sub>	335.7
3.	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	338.0
4.	C <sub>60</sub> Pd <sub>1</sub>	336.7
5.	C <sub>60</sub> Pd <sub>2.9</sub>	336.6
6.	C <sub>60</sub> Pd <sub>4.9</sub>	336.4
7.	Pd foil	335.3

the experimental investigation of the solid C<sub>60</sub> samples yields χ<sub>M</sub>(300K) = -210±40 per mole C<sub>60</sub>. But on the other hand, the theoretical consideration of the precession of 60 π-electrons yields χ<sub>M</sub> = -2000. The small experimental value arises from the paramagnetic (Van Vleck) contributions of the excited states, which almost completely suppress the diamagnetic contributions from the valence states. In the case of C<sub>60</sub> compounds one is inclined to think that the excited states are different from those in the free C<sub>60</sub>. Hence, we must consider two versions of the diamagnetic correction for η<sup>2</sup>-C<sub>60</sub> ligand in the complex. In I version we believe χ<sub>M</sub>(dia) = -210, thus taking into account the changes caused by complex formation. The II variant (χ<sub>M</sub>(dia) = -2000) allows one to isolate the paramagnetic part of the magnetic susceptibility of the complex.

In accordance with I variant the most like reason of the paramagnetic susceptibility of the complex is a very significant increase of Van Vleck contribution in η<sup>2</sup>-C<sub>60</sub> as compared with that for free C<sub>60</sub>. This interpretation is supported by the existence of the band at 613 nm in the absorption spectrum of the complex (this peak is located at 598 nm in the spectrum of free C<sub>60</sub>), by XPS data (see above), which can be considered as the evidence for the increase occupation of the excited states with high orbital moments and finally, by the absence of a signal in ESR spectrum with the intensity more than 10<sup>20</sup> spin per mole at T = 80-300K.

However, at the II variant the value μ<sub>eff</sub> is very close to the value, which is characteristic of two unpaired electrons (2.83 μ<sub>B</sub>), and we must think that the complex

under study is the Pd<sup>II</sup> compound, in which one unpaired electron is localized on  $\eta^2$ -C<sub>60</sub> ligand.

The XPS of Pd3d for C<sub>60</sub>Pd<sub>n</sub> is a doublet with rather narrow components typical of pure compounds (Fig.1). The position of the Pd3d<sub>5/2</sub> peak depends on n, viz. as n increases, E<sub>b</sub>(Pd3d<sub>5/2</sub>) decreases from 336.7 to 336.4 eV (Table). The comparison between these value and the analogous value for metallic Pd (335.3 eV) is indicative of the electron transfer from Pd to C<sub>60</sub>.

The correlation between the chemical shift of the XP peak and the effective charge on the corresponding atom is frequently violated by the effect of relaxation processes in the final state on the position peak. A charge in the modified Auger parameter  $\alpha'$  ( $\alpha' = E_b + E_{kin}$ , where E<sub>kin</sub> is the kinetic energy of the Auger electron formed in the decomposition of a state with a hole in the inner level) is proportional to the extraatomic relaxation energy R<sub>ex</sub>, viz.  $\Delta\alpha' = \Delta R_{ex}$ . To estimate  $\Delta R_{ex}$  we measured the positions of the Pd(M<sub>4.5</sub>N<sub>4.5</sub>N<sub>4.5</sub>) Auger peak in the binding energy scale for Pd foil and the C<sub>60</sub>Pd<sub>4.9</sub> polymer (926.1 and 927.2 eV, respectively). The values of  $\alpha'$  were calculated using the values of E<sub>b</sub>(Pd3d<sub>5/2</sub>) and were the same (662.8 eV) for metallic Pd and polymer. Consequently, the observed chemical shift of Pd3d<sub>5/2</sub> level on passing from metallic Pd to C<sub>60</sub>Pd<sub>n</sub> is caused only by a change in the effective charge on the Pd atom. The charge transfer from Pd to C<sub>60</sub> is also confirmed by the results of measurements of magnetic susceptibility the effective magnetic moment is 1.2  $\mu_B$  per formula unit of C<sub>60</sub>Pd<sub>4.9</sub>.

Fig.1 present the X-ray photoelectron valence band spectra of C<sub>60</sub>Pd<sub>4.9</sub> and metallic Pd. For the MgK $\alpha$  radiation, the photoionization cross-section of the Pd4d level is larger than that of the C2p level by more than 2 orders of magnitude. Therefore, in this energy range, the XPS substantially accounts for the distribution of 4d-electrons. These distributions for the metal Pd and C<sub>60</sub>Pd<sub>4.9</sub> are radically different. This shape of the distribution indicates that either Pd clusters are absent in the samples studied or their concentration is insignificant.

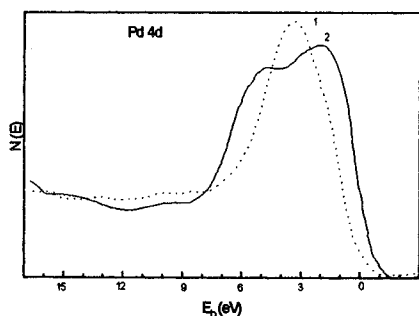


Figure 1. X-ray photoelectron valence band spectra of C<sub>60</sub>Pd<sub>4.9</sub> (1) and Pd foil (2).

The study demonstrated that the electron transfer from Pd to C<sub>60</sub> occurs in palladium fullerides; as a result, unpaired electrons appear in the system, which can give rise to magnetic and, primarily, ferromagnetic order in carbon system, as shown in fig.2. The mechanism of magnetic ordering is evidently kinematic, as described in [5]. The distribution of Pd in the sample is homogeneous or nearly homogeneous.

The reaction of D<sub>2</sub> with solid C<sub>60</sub>Pd<sub>4.9</sub> in the mild conditions (T=473-673 K, P<sub>D2</sub>=20 atm, 2h) yields fullerene deuterides (C<sub>60</sub>D<sub>x</sub>, x= 2, 4, 18 and 26) [5].

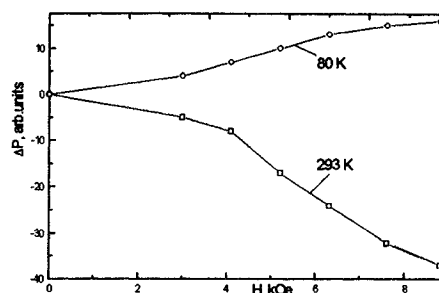


Figure 2. Weight of a diamagnetic container with a sample of C<sub>60</sub>Pd<sub>4.9</sub> as a function of external magnetic field (H).

## Conclusions

The investigation of the complex ( $\eta^2$ -C<sub>60</sub>)Pd(PPh<sub>3</sub>)<sub>2</sub> and palladium fulleride C<sub>60</sub>Pd<sub>n</sub> with n = 1-4.9 by the methods of X-ray photoelectron spectroscopy and magnetochemistry was demonstrated that the electron transfer occurs from Pd to C<sub>60</sub>.

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