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Optical spectra of Pd-561 nanoclusters in aqueous solutions

B. G. Ershov,[a★] **A. V. Gordeev,**[a] **M. N. Vargaftik,**[b] **I. P. Stolarov,**[b] **and I. I. Moiseev**[b]

[a]*Institute of Physical Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: +7 (095) 952 7514. E-mail: ershov@ipc.rssi.ru
[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 117907 Moscow, Russian Federation.
Fax: +7 (095) 952 1274. E-mail: mvar@ionchran.rinet.ru

Optical absorption spectra of aqueous solutions of the giant cluster $Pd_{561}Phen_{60}(OAc)_{180}$ (**1**) were studied in air and after treatment with H_2. The results obtained were compared with the corresponding data for 2—4-nm nanoparticles of colloidal palladium prepared by the radiochemical and chemical reduction of the Pd^{II} complexes in aqueous solutions. The optical spectra of cluster **1** and nanoparticles of colloidal palladium are of the same nature and are caused by the light absorption by free electrons in the metal.

Key words: palladium, nanoclusters, nanoparticles, colloids, optical spectra.

Optical spectra of nanoparticles of colloidal palladium were studied in Refs. 1—3. Theoretical calculations showed[1] that for spherical particles with sizes up to 10 nm the absorption spectra of free electrons in metal are the same and represent single bands with a maximum at 220±10 nm, which is monotonically shifted toward long wavelengths. When the size of the nanoparticles increases, this band is shifted to the visible region and becomes broadened, while the molar absorption coefficient decreases. The spectra of extended particles (rotation spheroids) exhibit an additional broad band, which is shifted to the longwave region with increasing the length of the long axis of the particle. Experimental studies of spherical palladium nanoparticles[2,3] confirmed the results of calculations. Sols with an average particle size of 2—4 nm prepared by the radiochemical or chemical (hydrogen) reduction of the Pd^{II} complexes in the presence of Na polyacrylate as a stabilizing agent are characterized by the absorption band with a maximum at 230 nm and a molar absorption coefficient (calculated per Pd atom) of $6.1 \cdot 10^3$ L mol^{-1} cm^{-1}.[3]

In this work, we studied the electronic absorption spectra of aqueous solutions of the giant cationic palladium cluster $[Pd_{561}Phen_{60}](OAc)_{180}$ (Phen is 1,10-phenanthroline) (**1**), whose composition and structure have previously[4—7] been established by the elemental analysis, atomic resolution electron microscopy, electron diffraction, EXAFS, magnetic susceptibility, and other methods. The metal skeleton of cluster **1** is formed by closely packed Pd atoms with the icosahedron and cubooctahedron structures and an average diameter of 2.5 nm.[5] The main purpose of this work is to reveal the electronic state of the metallic core of the giant clusters and colloidal palladium.

Experimental

Reagent grade chemicals were used. Cluster **1** was synthesized according to a previously described method[4] by the reduction (H_2) of palladium(II) acetate, which was pre-purified by refluxing in glacial AcOH with an additive of Pd black followed by recrystallization from AcOH. Solutions of cluster **1** were prepared by the weight method using bidistilled water. Solutions of colloidal palladium were prepared by the radiochemical or chemical (H_2) reduction of the palladium(II) complexes.[2,3]

Absorption spectra were recorded on a Shimadzu UV-3100 instrument using the cells with an optical path length of 1 cm at ~20 °C.

Results and Discussion

Optical spectrum of 1. Aqueous solutions of cluster **1**, as well as those of colloidal palladium obtained by the radiochemical or chemical (H_2) reduction of the Pd^{II} complexes using Na polyacrylate as a stabilizer,[2,3] are colored in intense dark-brown. The absorption spectra of $1 \cdot 10^{-4}$ *M* solutions of **1** and colloidal palladium are shown in Fig. 1. The spectrum of the latter is the difference between the total absorption spectrum of an aqueous solution of colloidal palladium and the absorption spectrum of Na polyacrylate ($5 \cdot 10^{-4}$ mol L^{-1}). The spectrum of colloidal Pd represents the absorption monotonically ascending to the UV region with a maximum at 230 nm ($\varepsilon = 6 \cdot 10^3$ mol L^{-1} cm^{-1}). The spectrum of a solution of **1** has a close intensity and the same smooth increase on going from the visible to UV region. However, unlike the spectrum of colloidal Pd, two weakly pronounced absorption bands belonging to Phen molecules are observed at $\lambda_1 = 223$ nm and $\lambda_2 = 275$ nm on the background of the total absorption

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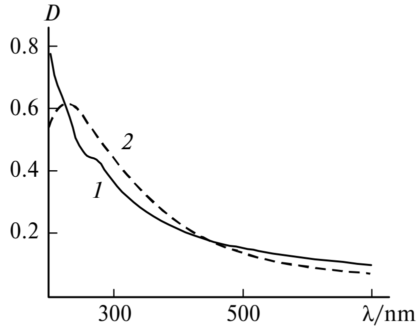

Fig. 1. Absorption spectra of $1 \cdot 10^{-4}$ *M* solutions of **1** (*1*) and colloidal Pd (*2*).

by the particles of **1**. In addition, the maximum at 230 nm characteristic of Pd nanoparticles of this size is absent, which is explained by the superposition in this spectral region of the additional absorption from the OAc^- ions contained in cluster **1**. In the concentration region from $1.0 \cdot 10^{-4}$ to $2.5 \cdot 10^{-3}$ mol L^{-1}, the shape of the absorption spectra remains unchanged, and the absorption intensity changes according to the Lambert—Beer law. This indicates that solutions of **1** manifest the properties of true solutions, and the giant clusters with an increase in the concentration do not form flocculas, associates, *etc.*

Thus, the absorption over the whole optical region with the intensity increasing smoothly toward the shortwave region, predominates in the spectrum of cluster **1**, which is typical of palladium nanoparticles. The spectral pattern is somewhat complicated by an additional absorption of the ligand molecules (Phen and AcO^-) contained in **1**. The optical absorption of palladium nanoparticles is due to the interband transitions and collective absorption of the electron gas (plasmons) in the spherical particles with a diameter <10 nm.[1] The spectrum changes substantially when the particle shape changes and their size increases. The absorption of **1** indicates the "metallic" state of Pd atoms, *i.e.*, that valent electrons exist in the unbound state typical of a metal.

State of Phen molecules on the surface of palladium nanoparticles. A comparison of the absorption spectra of Phen in an aqueous solution with that of Phen molecules coordinated on the surface of palladium nanoparticles indicates a substantial change in their state during the chemical interaction with surface metal atoms. The spectra of a $2.5 \cdot 10^{-4}$ *M* solution of **1** and a $2.7 \cdot 10^{-5}$ *M* solution of Phen (the concentrations corresponding to the stoichiometric content of Phen in cluster **1**) are shown in Fig. 2. It is seen that the binding of Phen molecules somewhat shifts the absorption bands (227 and 265 nm for free Phen and 223 and 275 nm for sorbed Phen) and decreases their intensity more than fivefold. The Phen ligands in **1** contribute slightly to the total absorption inherent in palladium nanoparticles.

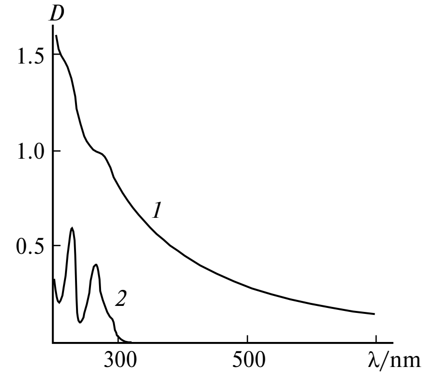

Fig. 2. Absorption spectra of $2.5 \cdot 10^{-4}$ *M* solutions of **1** (*1*) and a $2.7 \cdot 10^{-5}$ *M* solution of Phen (*2*).

In order to compare the nature of cluster **1** and nanoparticles of colloidal palladium in more detail, we studied the sorption of Phen by colloidal palladium. In these experiments, the absorption spectrum of a $2.5 \cdot 10^{-4}$ *M* solution of colloidal Pd containing $5 \cdot 10^{-4}$ mol L^{-1} of Na polyacrylate was recorded in time after the addition of a $2.7 \cdot 10^{-5}$ *M* solution of 1,10-phenanthroline (concentrations corresponding to the stoichiometric content of Phen in cluster **1**). The intensity of the absorption bands of free Phen decreases gradually with time (Fig. 3), and their position is shifted toward wavelengths characteristic of the palladium-bound state (227 and 265 nm for free Phen and 223 and 275 nm for sorbed Phen). After 24 h, the spectrum is similar to that of a solution of cluster **1** and further remains almost unchanged.

This result suggests that the final spectrum corresponds to the system in which Phen molecules exist in almost the same state coordinated to Pd atoms as in cluster **1**. The long time of equilibration of chemical binding of Phen with the surface of nanoparticles of colloidal Pd, which is not characteristic of standard sorption by metallic colloids, can be explained, most likely, by a slow diffusion of the Phen molecules through the protective polyacrylate layer accompanied, perhaps, by the rearrangement of the surface structure of the colloidal metal particles. From the chemical point of view, this process can be considered as the substitution

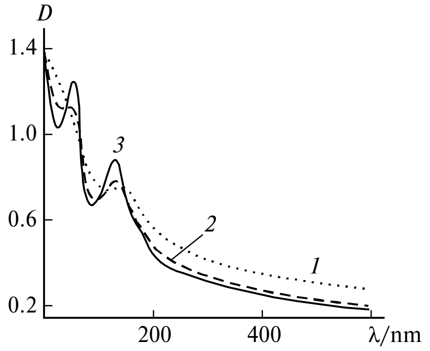

Fig. 3. Absorption spectra of a $2.5 \cdot 10^{-4}$ *M* solution of colloidal Pd in the presence of Na polyacrylate ($5 \cdot 10^{-4}$ mol L^{-1}) after the addition of Phen ($2.7 \cdot 10^{-5}$ mol L^{-1}): *1*, immediately after addition; *2*, 6 h after; and *3*, 24 h after.

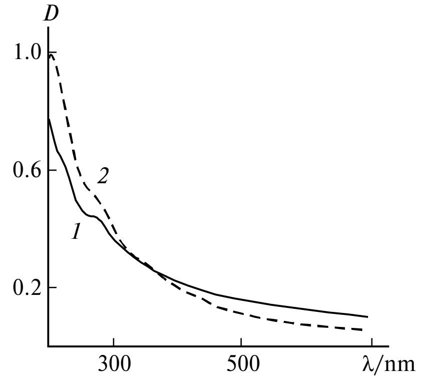

Fig. 4. Absorption spectra of $2.5 \cdot 10^{-4}$ *M* solutions of **1**: *1*, before treatment and *2*, after treatment with hydrogen (1 atm).

of some coordinated ligands, polyacrylate anions, by other, 1,10-phenanthroline molecules.

A substantial decrease in the intensity of optical transitions in the Phen molecules coordinated on the surface of Pd nanoparticles is probably due to the interaction of the conjugated π-electronic system of the aromatic Phen molecule with the electronic system of the positively charged metallic nanoparticle.

The observed changes in the optical characteristics of Phen during its sorption on the palladium nanoparticles, which are manifested as the shift of the bands and a considerable decrease in their intensity, is a general effect inherent in other aromatic molecules and their binding to the surface of metallic nanoparticles. Similar optical effects were observed for the sorption of Rhodamine B on the surface of silver nanoparticles[8] and of fluorescein isocyanate on gold nanoparticles.[9] Unlike palladium, both metals are characterized by individual absorption bands of plasmons (390 and 520 nm for Ag and Au, respectively). The changes in the intensity of these bands and their positions indicate a strong interaction of the aromatic molecules with free electrons of the metals.

Absorption of H_2 by Pd-561 nanocluster. It is known that palladium nanoparticles efficiently and reversibly absorb H_2 from the gas phase. The formation of hydrides is accompanied by the appearance of covalent interactions inside the metallic particle and changes their electron parameters, which is revealed in the optical spectra.[2,3] The maximum of the absorption band of colloidal Pd is shifted from 230 to 265 nm, and the intensity of the band decreases in the UV region and increases in the visible region.

We observed a similar effect for nanocluster **1**. The interaction of **1** with H_2 (1 atm) changes noticeably the absorption spectrum (Fig. 4). The absorption intensity decreases in the region of short wavelengths and, by contrast, increases in the visible region. These transformations are also reversible. After evacuation and admission of air, the spectrum returns to the original shape. Note that the intensity of absorption bands of Phen molecules in the spectrum of cluster **1** saturated with dihydrogen somewhat increases, which possibly indicates a weakening of the bond between these ligands and surface metal atoms.

Colloidal palladium, as cluster **1**, exhibits high catalytic activity in the hydrogenation of organic substrates.[4,10] The data obtained lend support to the assumption[4] that the catalysis of these reactions occurs, in fact, due to the hydride form of palladium nanoclusters rather than the metallic form.

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