

General and Inorganic Chemistry

Structure of polynuclear palladium(II) hydroxocomplexes formed upon alkaline hydrolysis of palladium(II) chloride complexes

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The structure of polynuclear Pd^{II} hydroxocomplexes (PHC) formed as a result of alkaline hydrolysis of Pd^{II} chloride complexes was studied by EXAFS, SAXS, and TEM methods. It is established that in aqueous solutions a hydroxocomplex particle is a filament curled into a ball containing about 100 Pd atoms. The filament consists of planar coordination squares of PdO₄ units linked *via* one or two oxygen bridges of different geometry. Aging of samples results in an increase in the number of single bridging ligands and a decrease in the diameter of particles. Interatomic distances around palladium atoms were determined.

Key words: palladium(II), hydrolysis, polynuclear complexes, EXAFS, SAXS, TEM, size distribution of particles.

We have shown previously¹ by UV and ¹⁷O, ²³Na, ³⁵Cl, and ¹³³Cs NMR spectroscopy that polynuclear hydroxocomplexes (PHC) [Pd(OH)₂]_n · mNaCl are the products of alkaline hydrolysis of palladium(II) chloride complexes. The structure of PHC was supposed to be formed by a linear polymer [Pd(OH)₂]_n curled into a ball in which individual polymer filaments are cross-linked by ions of alkaline metal *via* a bridging oxygen atom.¹

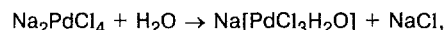
The results of studying the structure of PHC by transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and spectroscopy of extended X-ray absorption fine structure (EXAFS) are presented in this work.

Experimental

Preparation of samples. Analytical grade substances were used as initial reagents. Stock solutions of H₂PdCl₄, NaHPdCl₄,

and Na₂PdCl₄ were prepared by combined dissolution of stoichiometric amounts of PdCl₂, NaCl, and HCl in water. To study PHC, solutions of Na₂PdCl₄ were prepared to which a solution of NaOH was added to obtain the necessary χ value ($\chi = C_{\text{NaOH}}/C_{\text{Pd}}$, where C_{NaOH} and C_{Pd} are the concentrations of the alkali and Pd^{II} compounds, respectively, under the assumption that these two components do not react¹).

Since Pd^{II} chloride complexes undergo hydrolysis in aqueous solutions according to the scheme



an excessive (2 M) concentration of NaCl was introduced into solutions to suppress hydrolysis. All working solutions, except special cases, were prepared prior to measurements.

Tetraaquacomplexes [Pd(H₂O)₄]²⁺ were prepared by dissolution of the precipitate Pd(OH)₂, which was as-prepared and thoroughly washed of Na⁺ and Cl⁻ ions, in a 5 M solution of HClO₄. PdO was prepared by calcination of the Pd(OH)₂ precipitate for 4 h at 400 °C.

The concentration of palladium in stock solutions was controlled spectrophotometrically on a Specord UV-VIS instrument.

Transmission electron microscopy (TEM). Samples for TEM studies were prepared by sorption of PHC from solutions on a surface of hydrophilized graphite. The procedure of hydrophilization included ultrasonic dispersion of a graphite suspension in water, then concentrated acetic acid was added to the suspension, and it was kept for 10 h at room temperature. Then the suspension was washed with water to pH ~7 and repeatedly subjected to ultrasound, and a PHC solution studied was added to an aliquot of the suspension. Palladium was adsorbed with vigorous shaking for 10 min, although 2 min was enough to reach adsorption equilibrium (as established in special experiments).

The ratio between amounts of graphite and Pd^{II} compounds was chosen so as all palladium to be adsorbed from a solution. When adsorption was completed, samples were dried *in vacuo* at room temperature and ultrasonically sprayed onto a perforated carbon substrate.

Small-angle X-ray scattering (SAXS). An SAXS study was carried out in a KRM1 chamber (Cu-K α radiation, Ni-filter with amplitude discrimination, BSV22 tube, voltage 30 kV, current 40 mA). A solution studied was placed in a 1.5-mm tube with thin (20 μ m) Dacron windows. The size distribution of colloidal particles was calculated according to the previously described method.² All distribution curves presented were normalized to unity at a maximum.

Extended X-ray absorption fine structure (EXAFS). An EXAFS study was carried out on an SI spectrometer³ (Siberian Center of Cyclotron Resonance) according to the transmission procedure. A double monounit Si(111) crystal-monochromator was used for monochromating radiation. PdK absorption spectra were recorded in steps of 1.5 eV. Spectra were treated by Fourier analysis. An oscillating component was isolated according to the standard procedure.³ A preedge region was extrapolated to an EXAFS region by Viktorin type polynomials. An inflection point at the edge of the absorption jump was taken as E_0 .

A smooth region was plotted as cubic splines with an additional frequency filtration of residues of the smooth region with smoothing splines. The Fourier transformation was performed for the oscillating component of the absorption spectrum multiplied by K^1 and K^3 in the 3.5–14.0 \AA^{-1} range of wave numbers. Interatomic distances around palladium atoms were interpreted by comparing them with those for the compounds of known structures.

To study samples, which are prone to precipitation from solution, a suspension of a sample was poured into agar-agar gel heated to 30–40 $^{\circ}$ C. After solidification of the gel, the

samples could be aged without precipitation. It was shown in special experiments that EXAFS spectra of pure (without fixation) as-prepared samples and the same samples fixed in agar-agar did not differ.

Results and Discussion

Electron microscopy. Since palladium compounds were sorbed from a solution on the graphite surface during preparation of samples for TEM, a question arises about the possibility of formation of polynuclear Pd^{II} complexes from mononuclear complexes in the process of their interaction with graphite. To check this assumption, samples prepared by adsorption of Pd^{II} from solutions containing H_2PdCl_4 and Na_2PdCl_4 were studied. No particles observed by TEM with the maximum magnification of the instrument, *i.e.*, particles ≥ 3 \AA , were observed in the samples containing 0.2 % of Pd. Therefore, mononuclear complexes did not originate from the polynuclear structures observed.

The TEM patterns for the samples with $\chi = 0.2$ (Fig. 1, *a*) show the particles of 5 to 80 \AA in diameter, and large particles are associates of smaller particles. The majority of the particles are 8–12 and 20–24 \AA in diameter (Fig. 2, histogram *a*). An increase in χ (Fig. 1, *b*) of solutions results in an increase in concentration of polynuclear complexes in solution, which can be estimated by an increase in the number of particles observed on the unit graphite surface (when a content of palladium in initial samples is constant). The size distribution of particles remains almost unchanged as χ increases (Fig. 2, *b*).

Aging of PHC solutions for 2 h before adsorption on graphite does not change both the surface concentration of PHC particles on graphite and their size distribution (Fig. 2, *c*). The latter point was checked by the statistical analysis of histograms presented in Fig. 2.

Small-angle X-ray scattering. Figure 3 presents curves of the change in size distribution of PHC particles in solutions with $\chi = 0.4$ as they are aging. It is of interest that shapes and positions of maxima of curves obtained

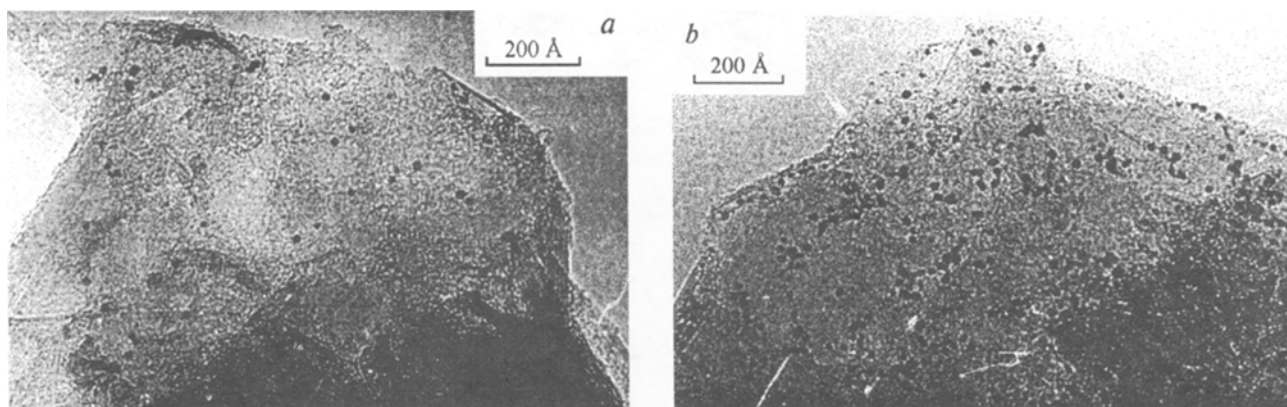


Fig. 1. TEM patterns of PHC sorbed on graphite; *a*, $\chi = 0.2$; *b*, $\chi = 0.65$.

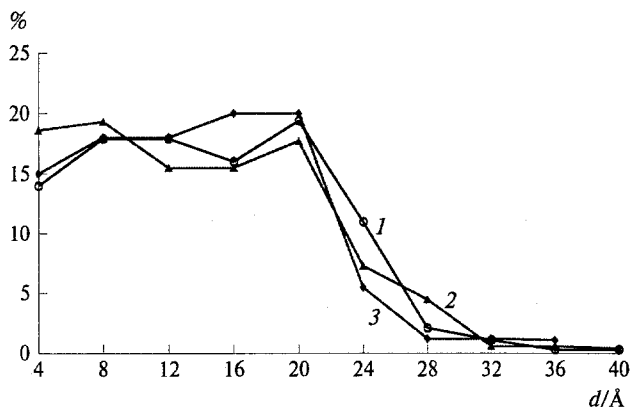


Fig. 2. Size (d) distribution of PHC particles sorbed on graphite according to TEM data; 1, $\chi = 0.2$; 2, $\chi = 0.65$; 3, $\chi = 0.65$; solution was aged for 2.5 h before adsorption.

for as-prepared solutions with $\chi = 0.2$ and 0.6 nearly coincide with those of curve 1 in Fig. 3. This confirms the TEM data supporting the fact that the size distribution of PHC depends slightly on the χ value. It can be seen from Fig. 3 (curve 1) that the majority of particles have a narrow distribution, whose maximum falls on particles with a diameter of 36 Å. In addition to this peak, distribution maxima corresponding to particles ~90 and ~130 Å in diameter are observed. Such sizes are typical of associates consisting of a central particle 36 Å in diameter surrounded by one (90 Å) or two (130 Å) layers of particles 36 Å in diameter.

Aging of solutions results in a decrease in sizes of PHC (see Fig. 3, curves 2 and 3). Diameters of fine particles decrease to ~28 Å, and the size of associates depends on duration of aging. For example, particles 80 and 130 Å in diameter observed in 24 h in 2.5-h aged solutions transform to particles 75 and 120 Å diameter, respectively.

It should be mentioned that particle sizes determined by SAXS are considerably larger than those obtained by TEM (cf. 18–20 Å according to TEM data and 28 Å by SAXS data). The reason for this difference could be the

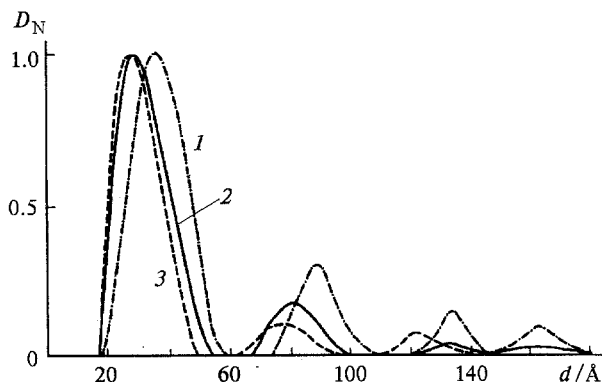


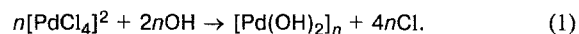
Fig. 3. Size (d) distribution of PHC particles in solutions with $\chi = 0.4$ according to SAXS data; 1, as-prepared solution; 2, 2.5-h aged solution; 3, 24-h aged solution. $C_{Pd} = 0.1 \text{ mol L}^{-1}$.

fact that the TEM method observes clusters of $[\text{Pd}(\text{OH})_2]_n$ type formed by Pd^{2+} ions, while Na^+ and Cl^- ions entering solvate shells of the clusters are not seen against a background of the substrate. The SAXS method observes objects with electron density differing from that of a medium, in this case, it is a solution without clusters. Such an area can include not only palladium cluster, but its solvate shell as well. In addition, a decrease in particle sizes in samples for TEM can be related to the formation of samples of palladium(II) compounds sorbed on graphite as compact crystalline structures. These structures can be formed during drying of samples.

The change in distribution of primary particles is completed during 2.5 h of aging of solutions (average diameter is 28 Å), while the average diameter of particles of associates decreases for a long time (see Fig. 3, curves 2 and 3), accompanied, as measurements show, by a decrease in the pH of the solutions. It is likely that solvate shells between particles in associates are decomposed to form uniform globules.

EXAFS. To determine distances between the central Pd atom and the ligands of the first coordination sphere, EXAFS spectra of both aqueous solutions of H_2PdCl_4 , Na_2PdCl_4 , and $\text{Pd}(\text{aq})_4^{2+}$ complexes and solid samples of $\text{Pd}(\text{OH})_2$, PdO , and $\text{Pd}(\text{OAc})_2$ were obtained. The distances found by EXAFS are the following: Pd—Cl 2.25 Å ($R - \delta = 1.85$ Å) and Pd—O 2.0 Å ($R - \delta = 1.5$ Å), where R is the interatomic distance and δ is the correction coefficient, which is 0.5 Å for O and Cl atoms and 0.25 Å for Pd. These values coincide with distances available in reference literature.⁴

The EXAFS spectrum of the solution with $\chi = 1$ is presented in Fig. 4 (curve 1). This solution contains Pd complexes in which the central atom is surrounded by both chloride and oxygen-containing (O^{2-} , OH^- , or H_2O) ligands. It is impossible to distinguish complexes, in which the central Pd atom is surrounded by either Cl or O atoms, by this method. However, it has been shown previously¹ that alkaline hydrolysis occurs *via* the equation:



All unreacted palladium remains in the form of $[\text{PdCl}_4]^{2-}$ complexes, while reacted palladium does not contain Cl^- ligands and enters PHC. Therefore, the signals of ligands of the first coordination sphere observed in the EXAFS spectrum were assigned to the signals from Pd—Cl distances in complexes $[\text{PdCl}_4]^{2-}$ and Pd—O distances in PHC. Cl^- ligands are coordinated only with Pd of mononuclear complexes, and oxygen-containing ligands enter PHC. Two additional intense peaks with $R - \delta = 2.4$ Å and $R - \delta = 2.9$ Å are observed in the spectrum in Fig. 4 (curve 1). We failed to find such values of interatomic distances in the literature on X-ray studies of palladium compounds. Therefore, to assign these distances, models of PHC with possible arrangement of planar coordination squares

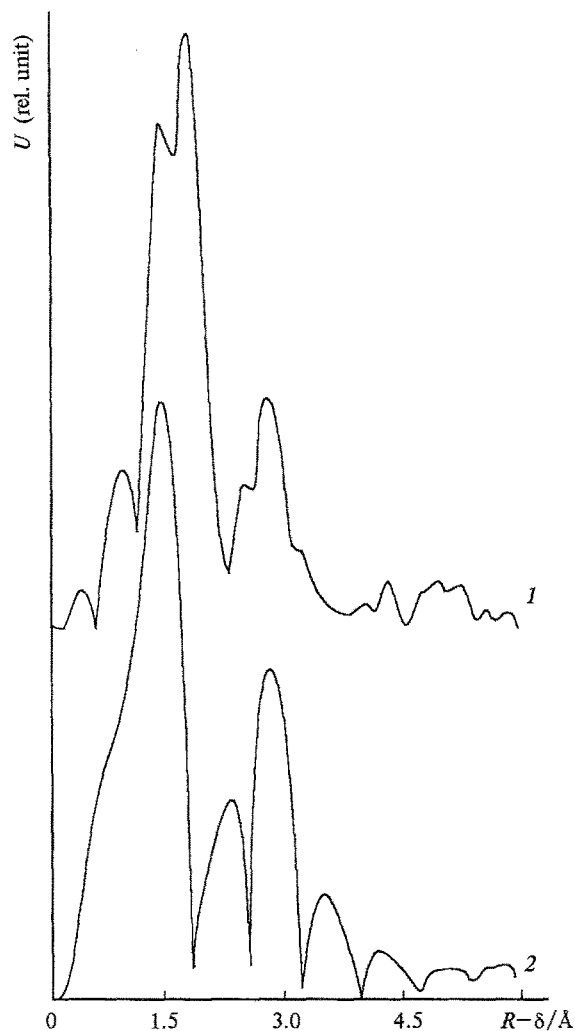


Fig. 4. Fourier transformation of EXAFS spectra; 1, $\chi = 1$, $C_{\text{Pd}} = 0.2 \text{ mol L}^{-1}$; 2, $\chi = 2$, agar-agar.

PdO_4 were developed. The fragment of the PHC structure that best fits EXAFS data is presented in Fig. 5. Palladium atoms are coordinated with oxygen atoms of two types. The first type is presented by oxygen atoms of the bridging ligands (O(3), O(4) in Fig. 5), which are linked to neighboring Pd atoms by two oxygen bridges. In this case, the Pd(1)—O(3)—Pd(2) angle is 90° , and the Pd(1)—Pd(2) distance is 2.65 \AA ($R - \delta = 2.4 \text{ \AA}$). Oxygen atoms of the second type are linked with two Pd atoms by one bridge. The Pd(2)—O(6)—Pd(3) angle is equal to 106° (which is close to the value of the H—O—H angle in a water molecule), and the Pd(2)—Pd(3) distance is 3.2 \AA ($R - \delta = 2.95 \text{ \AA}$).

An additional argument in favor of the structure presented in Fig. 5 is the fact that all EXAFS spectra for 30 PHC samples studied, which differ in composition and "biography", contain the peaks with $R - \delta = 4.1 \text{ \AA}$ and $R - \delta = 4.4 \text{ \AA}$. These peaks are beyond the region of exact measurements, which is determined by the signal/noise ratio. However, the fact that many spectra

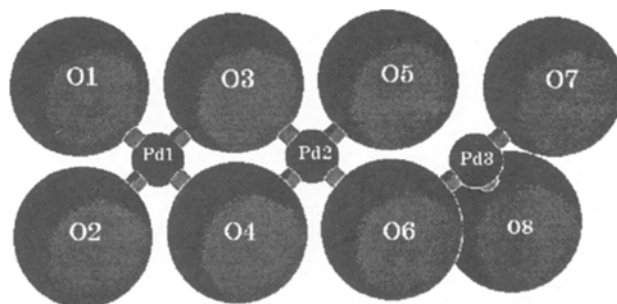


Fig. 5. Fragment of the PHC polymer chain. The model was designed taking account of the crystal chemical radii of Pd^{2+} and O^{2-} ions. The O(9) atom (at the *trans*-position to O(8)) is removed. Interatomic distances are given in text.

contain them allows us to believe that the corresponding distances exist in the PHC structure. The distances Pd(1)—O(6) 4.6 \AA ($R - \delta = 4.1 \text{ \AA}$) and Pd(2)—O(7) 4.9 \AA ($R - \delta = 4.4 \text{ \AA}$) correspond to these peaks in the model presented in Fig. 5.

The EXAFS spectra obtained for solutions with various χ values differ from the spectrum presented above only in the ratio of the intensities of peaks. Estimation of intensities of peaks of the ligands of the first coordination sphere made it possible to determine the number of Cl^- ions bound to palladium. It has been established that when $\chi = 0.25$, $\sim 90\%$ of the initial Cl^- ligands remain coordinated to Pd; when $\chi = 0.5$, $\sim 30\%$; when $\chi = 1$, $\sim 50\%$; and when $\chi = 2$, solutions contain almost no coordinated chloride ligands. The values obtained agree well with the previously obtained results¹ and Eq. (1) for hydrolysis.

The spectrum of a $\text{Pd}(\text{OH})_2$ suspension obtained by the reaction between 1 eqv. of Na_2PdCl_4 and 2 eqv. of NaOH is presented in Fig. 4 (curve 2). Two-week aging of this suspension fixed by agarose results in some increase in the intensity of the peak with $R - \delta = 2.95 \text{ \AA}$, which is likely related to gradual rearrangement of the filament-like structure of palladium hydroxide to the three-dimensional structure of its oxide. The latter structure comprises stacks of coordination PdO_4 squares (see Ref. 4). The rearrangement is accompanied by a decrease in the number of double oxygen bridges, which allows more compact curling of the filament-like structure of PHC. It is noteworthy that such a rearrangement should be accompanied by a decrease in pH of solutions mentioned above, because neighboring Pd atoms should contain one bridging and one terminal ligand instead of two bridging OH^- ligands. The source of additional OH^- ligands is dissociation of water followed by evolving H^+ . The intensity of the peak of O ligands of the first coordination sphere of Pd during aging of the suspension remains unchanged, and there is no peak of Cl^- ligands not only in aged $\text{Pd}(\text{OH})_2$ samples, but in freshly prepared samples as well. This fact testifies that the hydrolysis followed by the formation of PHC is fast and irreversible.

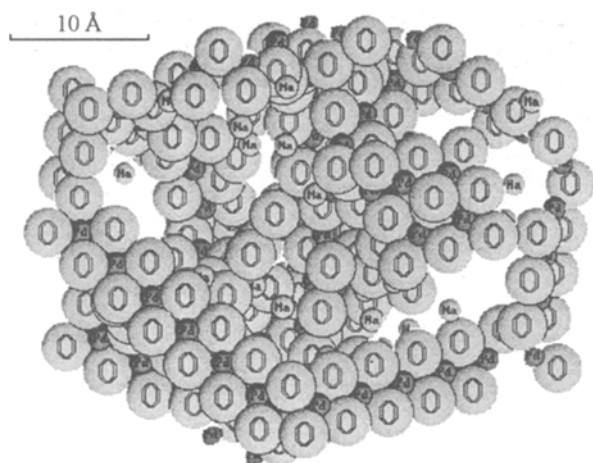


Fig. 6. Model of the PHC particle.

Certain conclusions about the structure of PHC can be made on the basis of the data obtained by various methods. The model of such a structure formed by curling of one chain of fragments (see Fig. 5) and containing 100 Pd atoms is presented in Fig. 6. Planar coordination PdO_4 squares are linked by one or two bridging O ligands to form a filament. Single bridges provide mobility of the filament, allow it to be curled into a compact particle, and are a reason for appearance of branches. Individual regions of the filament are drawn together (probably due to the $\text{Pd}_2\text{O}-\text{Na}^+-\text{OPd}_2$ inter-

action) involving ions of alkalis, whose presence in the PHC structure has been shown previously.¹ Aquated Cl^- ions surround a particle to compensate its charge.

A stable particle contains (as the model presented in Fig. 6) about 100 palladium atoms, which corresponds to the diameter of a compact globule (20 Å) observed by TEM. Cavities and linear regions of $\text{Pd}(\text{OH})_2$ in the structure result in some porosity of particles, provide the possibility of decreasing their diameter upon aging, and are a possible reason for disagreement between TEM and SAXS data.

Aging is accompanied by evolving H^+ ions to a bulk solution: double OH^- bridges are replaced with single bridges. In the case of a long aging or drying the suspension, water, and H^+ and Cl^- ions should be released from the PHC globules, because this results in formation of a compact crystalline structure of PdO .

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