If one assumes that the cation content is determined by the number of electrons located in the S-Mo-S layers at the moment of formation of the intercalation compounds in the solution, one can conclude that this quantity reaches the value of about  $1/3 e^-$  per Mo atom for the freshly prepared dispersion. One has to note also that all powdered intercalation compounds obtained by us are first stage compounds (i.e., they contain an intercalant in each van der Waals slit of a layered crystal) and do not contain a phase of nonintercalated  $MoS_2$ . This indicates that complete separation of compounds S-Mo-S layers is attained in the aqueous dispersion of which these compounds are formed.

If the replacement of Li cations by cations with a lesser solvation capacity drastically lowers the stability of the Li<sup>+</sup>-H<sub>2</sub>O-(MoS<sub>2</sub>)<sup>-</sup> ionic system, as described above, then the introduction of molecules that are capable of forming strong solvation complexes with Li ions would lead to the opposite effect. In fact, the addition of THF (up to 30 % v/v) or glycerol (up to 50 % v/v) to the aqeous monolayer MoS<sub>2</sub> dispersion leads to an increase of up to one week in the time interval which is necessary for spontaneous sedimentation to complete. The interlayer distances in the  $\text{Li}_x(\text{solv})_y\text{MoS}_2$  intercalation compounds (c = 11.0 Å for THF and c = 12.3 Å for glycerol) thus formed differ from those observed upon spontaneous aggregation of the aqueous dispersion, which is indicative of the solvation of Li ions with organic molecules in the interlayer space.

Thus, the results obtained in this work indicate that the S-Mo-S layers in a aqueous monolayer  $MoS_2$  dispersion have a negative charge and form ion pairs with hydrated Li cations. This allows one to synthesize hitherto inaccessible intercalation compounds of  $MoS_2$  with organic and inorganic cations by ion-exchange reactions.

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# Studies of the compositions of Pd(II) hydrolysis products

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The characterization of the clusters formed on alkaline hydrolysis of  $[PdCl_4]^{2-}$  was performed using <sup>17</sup>O, <sup>23</sup>Na, <sup>35</sup>Cl, <sup>133</sup>Cs NMR and UV spectroscopy. The chemical composition of the clusters was found to be  $[Pd(OH)_2]_n \cdot n$ NaCl. No mononuclear oxo- or hydroxocomplexes were detected. The spatial structure of the clusters is stabilized by alkali metal cations.

Key words: palladium(II), hydrolysis, polynuclear complexes, NMR, UV spectroscopy.

Hydrolysis of palladium salts is the subject of a number of studies.<sup>1-7</sup> The information on the composition of Pd(II) hydrolysis products is incomplete, and the data available are often contradictory. Polynuclear hydroxocomplexes (PHC) resulting from hydrolysis have received only occasional attention.

With NaCl used as the supporting electrolyte, the polymeric products of the alkaline hydrolysis of  $H_2PdCl_4$  were shown by pH-metric titration to be  $[Pd(OH)]_n^{n+1}$  complexes (with no account of the components of the medium). The average number (*n*) of PdOH units in the polymeric chain increases with increasing Pd concentra-

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tion and decreasing NaCl concentration. Data processing using the program «Letagrop» allowed us to conclude that complexes  $[PdOH]^+$  and  $[PdOH]_4^{4+}$  dominate under these conditions. Our data<sup>2</sup> on the composition of PHC obtained by pH-metric titration coincide with those published earlier.<sup>1</sup>

Upon hydrolysis of Pd(II) salts at pH < 2 in the presence of  $HClO_4^3$ , aquacomplexes  $[Pdaq]^{2+}$ ,  $[Pd(OH)aq]^+$ , and  $[Pd(OH)_2aq]$  were registered in the solution; no PHC formation was observed.

Physico-chemical studies (dialysis, solubility, ion exchange) of the products of Pd(II) hydroxide dissolution in  $HClO_4$  revealed the minimum number of Pd atoms in stable PHC to be six under these conditions.<sup>4</sup> The formation of larger complexes is still questionable because of insufficient measurement accuracy.

The presence of colloid particles in aqueous solutions of Pd(II) salts at pH 5-6 was reported in ref. 5.

Studies of alkaline hydrolysis of  $H_2PdCl_4$  (measurements of pH, pCl, and solution light scattering)<sup>6</sup> have shown that Pd(II) complexes contain 2.7 Cl<sup>-</sup>-ligands per Pd atom at pH < 3; PHC containing up to 10 palladium atoms at pH 3 and particles involving more than 1000 Pd atoms at pH 3.5 were observed. At the end of titration the precipitate had a composition Pd(OH)<sub>16</sub> Cl<sub>0.4</sub> · 0.1NaOH.

Pd(OH)<sub>1.6</sub> Cl<sub>0.4</sub>  $\cdot$  0.1NaOH. [Pd(OH)<sub>4</sub>]<sup>2-</sup> complexes are presumably formed in an alkaline medium (cf. ref. 7).

We have studied the alkaline hydrolysis of Pd(II) compounds using physicochemical methods which have not been employed for this purpose so far.

#### Experimental

Reagents of «analytical» purity grade and HCl of «special» purity grade were used in the work. A solution of  $H_2PdCl_4$  was prepared by dissolving the calculated amounts of PdCl<sub>2</sub> and HCl in water. The Pd concentration in the stock solution was determined by flame absorption spectroscopy. The overall concentration of Cl<sup>-</sup> ions was determined by potentiomentry: the Pd(II) compounds were reduced to the metal by sodium formate, and then Cl<sup>-</sup> ions were titrated with a silver nitrate solution.

Assuming the absence of chemical interaction between the solutes, hereinafter we indicate the overall concentrations of Pd(II), OH<sup>-</sup>, and Cl<sup>-</sup> as C<sub>Pd</sub>, C<sub>OH</sub>, and C<sub>Cl</sub>, respectively, and their equilibrium concentrations, as [Pd], [OH<sup>-</sup>], and [Cl<sup>-</sup>], respectively. Additionally, a parameter « $\chi$ » is introduced,  $\chi = C_{OH}/C_{Pd}$ . Then, a solution with  $\chi = 0$  corresponds to a solution of Na<sub>2</sub>PdCl<sub>4</sub>.

Solutions with various  $\alpha \chi \gg \alpha$  values were prepared by slow addition of the required amounts of NaOH to the solution of H<sub>2</sub>PdCl<sub>4</sub> with vigorous stirring.

<sup>2</sup> An ÈV-74 ionometer equipped with a platinum electrode (Cl<sup>-</sup> analysis) and a glass electrode (pH control) was used for titrimetric analysis.

Electron absorption spectra were employed to identify mononuclear complexes of palladium (II) in solutions with different  $\chi$  and  $C_{\rm Pd}$  values (Specord UV-VIS spectrometer).<sup>7</sup> Both standard (1-5 mm) and special thin-layer (*ca.* 0.01 mm) cells for solutions with high Pd concentrations were utilized in the experiments.

<sup>17</sup>O, <sup>35</sup>Cl, <sup>23</sup>Na and <sup>133</sup>Cs NMR spectra were recorded at 40.7, 29.4, 14.0, and 39.36 MHz, respectively, with 5–200 ms delay (Bruker CXP-300 spectrometer). Chemical shifts (CS) in the  $\delta$ -scale (a positive shift is that to lower field) were referred to external standards (H<sub>2</sub>O, 1 *M* NaCl, and salt solutions containing the corresponding cations) extrapolated to infinite dilution.

The concentration of free Cl<sup>-</sup> ions was determined using <sup>35</sup>Cl NMR spectra: Cl<sup>-</sup>-ions coordinated to palladium are not observed due to line broadening through the quadrupole mechanism of NM-relaxation. With <sup>17</sup>O NMR it is possible to detect the OH<sup>-</sup> and H<sub>2</sub>O ligands coordinated to Pd(II); their CS in complexes H<sub>2</sub>O-Pd-H<sub>2</sub>O (-112 ppm), H<sub>2</sub>O-Pd-Cl (-86 ppm), and HO-Pd-HO (-98 ppm) have been determined before.<sup>9</sup>

The <sup>23</sup>Na and <sup>133</sup>Cs NMR spectra were recorded to characterize the changes in the NMR parameters of counterions, which are used to detect negatively charged colloid particles formed in the course of hydrolysis.<sup>10</sup> Cs<sup>+</sup> cations were added to the solutions as CsCl or CsOH in trace amounts compared to those of the major components.

Data on the effect of the nature and the concentration of the components on the CS of <sup>133</sup>Cs were obtained in preliminary experiments. Thus, for Cs salts with counterions Cl<sup>-</sup>,  $[PdCl_4]^{2-}$ , and  $[Pd(OH)_4]^{2-}$  the CS of <sup>133</sup>Cs were found (with extrapolation of the anion concentrations to 1 *M*) to be  $\Delta = -11$ , -40, and -130, respectively.

In addition, the content of Na<sup>+</sup> ions was determined in the precipitate after the H<sub>2</sub>PdCl<sub>4</sub> solution had been titrated with NaOH to  $\chi = 2$ . To<sup>2</sup> this end, Na<sup>+</sup> concentration in the solution separated from the precipitated palladium hydroxide was estimated with the help of <sup>23</sup>Na NMR.

#### **Results and Discussion**

The dependence of the concentration of free chloride ions (referred to gramm-atom of Pd(II)) on  $\chi$  was obtained by <sup>35</sup>Cl NMR (Fig. 1). The curves for the two  $C_{Pd}$  values differ only in the initial ( $\chi \rightarrow 0$ ) region. Midregions of the plots are linear, and the number of Cl<sup>-</sup> ions which result from the introduction of one OH<sup>-</sup> group calculated from the slope is two. Complete replacement of chloride by hydroxo ligands occurs at  $\chi \approx 2$ . In this case only traces of Pd remain in the supernatant, and the precipitate was shown by measuring [Cl] to contain 1 mol of Cl<sup>-</sup> per 1 mol of Pd(II). No changes in this ratio were observed after the palladium hydroxide suspension was aged ( $\chi = 2$ ) for one hour.

At  $\chi = 1$  the concentration of Cl<sup>-</sup> was found to be constant between 5 min and 2 hours after preparation of the solution, though the pH decreased by one during this interval.

The divergence of titration plots (Fig. 1) in the initial region results from the fact that the alkaline hydrolysis of palladium compounds itself is accompanied by their autohydrolysis as follows:

$$[PdCl_4]^{2^-} + H_2O \rightarrow [PdCl_3(H_2O)]^- + Cl^-.$$
(1)



Fig. 1. Relative concentrations of Cl<sup>-</sup> in solutions with various  $\chi$  values.  $C_{Pd} = 0.5$  M (1), 0.25 M (2).



On the whole, the <sup>35</sup>Cl NMR data can be accounted for by the fact that some of the Cl<sup>-</sup> ligands split off from Pd remain in PHC particles in the adsorbed state, probably, as a component of a double electric layer.

Ultraviolet spectroscopy. Hydrolysis of Pd(II) compounds was carried out both in the presence of the supporting electrolyte and in its absence. A 2 M NaCl solution was employed as the supporting electrolyte, since both the ions were already present in the initial Na<sub>2</sub>PdCl<sub>4</sub> solutions.

Studied first were the changes in the UV spectra as a function of  $C_{Pd}$  (10<sup>-4</sup>  $M < C_{Pd} < 1 M$ ). Absorption bands at 45,000, 35,800, and 21,100 cm<sup>-1</sup> which are characteristic of  $[PdCl_4]^{2-}$  ions,<sup>8</sup> were observed in all of the solutions. No mononuclear Pd(II) complexes containing OH<sup>-</sup> and H<sub>2</sub>O ligands were found. The qualitative difference between the spectra at various  $\chi$  values consists of an increase in «background» absorption with  $\chi$ . This is most pronounced at 27,000 cm<sup>-1</sup> (Fig. 2, curves *I* and *2*). The «background» absorption decay in the longwave region of the spectra suggests radiation dispersion by colloid PHC particles (similar to Rayleigh dispersion), as was observed earlier.<sup>6</sup>

Note that no absorption bands differing from those of  $[PdCl_4]^{2-}$  ions were found over all of the measurement ranges of  $C_{Pd}$  and  $\chi$ :  $10^{-3}$   $M < C_{Pd} < 2$  M;  $0 < \chi < 2$ .  $[PdCl_4]^{2-}$  concentration was found from its  $\chi$ -dependence to be halved (Fig. 3) upon addition of one OH<sup>-</sup> group per palladium atom in the solution. Therefore, to bind one palladium atom into PHC, two OH<sup>-</sup> ions are needed, and the PHC composition (without



Fig. 2. UV spectra of Pd(II) solutions in the presence (1, 2) and in the absence (3, 4) of the supporting electrolyte.  $C_{\text{Pd}} = 0.5 M (1, 3), 10^{-3} M (3, 4); \chi = 0 (1, 3), 0.5 (4), 1 (2);$  $C_{\text{NaCl}} = 2 M (1, 2).$ 

Cl<sup>-</sup>, H<sub>2</sub>O, and Na<sup>+</sup> involved) can be formulated as  $[Pd(OH)_2]_n$ .

Although solutions with high  $\chi$  value are unstable over time, no considerable changes occurred during spectrum recording (*ca.* 3 min).

Without the supporting electrolyte there are  $[PdCl_4]^{2^-}$ complexes in solutions with  $C_{Pd} > 0.1 \ M$ . The absence of an excess of Cl<sup>-</sup> ions results in the appreciable hydrolysis of  $[PdCl_4]^{2^-}$  upon dilution of the solution with water according to Eq.(1). This is manifested in the spectra (Fig. 2, curve 3) by the bands at 41,800, 31,800, and 23,200 cm<sup>-1</sup>, which are characteristic of the  $[PdCl_1(H_2O)]^-$  complex.<sup>8</sup>

Addition of alkali to solutions of Na<sub>2</sub>PdCl<sub>4</sub> with high Pd concentration (0.1–1 *M*) also causes the appearance of «background» absorption which increases with  $\chi$ . In this case, as in the presence of the supporting electrolyte, mononuclear complexes are not observed except for [PdCl<sub>4</sub>]<sup>2-</sup>; the [PdCl<sub>3</sub>H<sub>2</sub>O]<sup>-</sup> bands are detected only when the solution is diluted to  $C_{Pd} = ca. 10^{-3} M$  (Fig. 2, curve 4). As  $\chi$  increases, higher dilution is needed, because autohydrolysis is inhibited by Cl<sup>-</sup> generated in the course of alkalization. At the same time, a peak of water with CS = -86 ppm, which corresponds to the Cl-Pd-H<sub>2</sub>O coordination,<sup>9</sup> is observed by <sup>17</sup>O NMR in the initial Na<sub>2</sub>PdCl<sub>4</sub> solution, which indicates a considerable concentration of the [PdCl<sub>3</sub>H<sub>2</sub>O]<sup>-</sup> complex. Note that, judging by <sup>195</sup> Pt NMR data, more than 10 %



Fig. 3. Concentration of  $[PdCl_4]^{2-}$  versus  $\chi$ ,  $C_{Pd} = 0.02 M$ ;  $C_{NaCl} = 2 M$ .

of the Pt(II) in a 0.3 M solution of  $K_2$ PtCl<sub>4</sub> is incorporated in the [PtCl<sub>3</sub>H<sub>2</sub>O]<sup>-</sup> complex.<sup>11</sup>

Surveying the UV data obtained, we can conclude that PHC are the products of alkaline hydrolysis of  $[PdCl_4]^{2-}$ , whereas  $[PdCl_3H_2O]^{-}$  is formed as a result of autohydrolysis according to equation (1). With <sup>35</sup>Cl NMR data taken into account, the following equation can be suggested for the alkaline hydrolysis:

$$n[\mathrm{PdCl}_4]^{2^-} + 2n\mathrm{OH}^- \rightarrow [\mathrm{Pd}(\mathrm{OH})_2]_n + 4n\mathrm{Cl}^- .$$
<sup>(2)</sup>

In this equation the alkali metal cations and water molecules which might be the components of PHC are not taken into consideration, and n is so great that PHC exhibits properties of colloid particles.

In the <sup>17</sup>O NMR spectra of the initial Na<sub>2</sub>PdCl<sub>4</sub> solution a peak at -86 ppm is observed. This peak was previously attributed to  $H_2O-Pd-Cl$  coordination of the [PdCl<sub>3</sub>H<sub>2</sub>O]<sup>-</sup> complex.<sup>9</sup> The addition of alkali ( $\chi =$ 0.1) results in broadening and weakening of this peak, and it disappears at  $\chi = 0.2$ . This is accounted for by the shift of the equilibrium (1) to the left owing to Cl<sup>-</sup> ions evolved into the solution. No appreciable amounts of mononuclear palladium complexes with oxygen ligands are shown by UV spectroscopy to be formed here. Again, upon acidification of an alkaline  $Na_2[Pd(OH)_4]$ solution with HCl these mononuclear complexes are also not found. In the <sup>17</sup>O NMR spectrum of the starting solution there is a peak at -101 ppm which is attributed to the oxygen atoms coordinated with OH-Pd-OH.9 When the solution is acidified to pH 9, weakening and broadening of this peak are observed, and at pH 8 it disappears. At pH 2 [PdCl<sub>4</sub>]<sup>2-</sup> complexes are formed. Only the water peak is observed in the <sup>17</sup>O



Fig. 4. <sup>133</sup>Cs NMR for solutions with  $C_{\rm Pd} = 0.2 M$ ,  $C_{\rm Cs} = 0.07 M$ . *a* — Chemical shift as a function of  $\chi$  in solutions without

a — Chemical shift as a function of  $\chi$  in solutions without supporting electrolyte (1) and those containing 2 *M* NaCl (2).  $b - 1^{33}$ Cs NMR spectrum of the solution without supporting electrolyte,  $\chi = 1.45$ .

NMR spectrum of the suspension of  $Pd(OH)_2$  precipitated.

On the whole, the results obtained can be rationalized by formation of colloid PHC particles as hydrolysis products. The fragments of these particles, PdOH, do not build up strongly ordered structures.

Figure 4 demonstrates changes in the <sup>133</sup>Cs NMR spectra during titration of Na<sub>2</sub>[PdCl<sub>4</sub>] by NaOH. CS is seen to increase linearly within the range of  $0 < \chi < 1.2$ , which can be attributed to the replacement of Cl<sup>-</sup> ligands coordinated to palladium with OH<sup>-</sup>, as [Pd(OH)<sub>4</sub>]<sup>2-</sup> causes a greater shift of the <sup>133</sup>Cs NMR line than [PdCl<sub>4</sub>]<sup>2-</sup> does (see above). However, the change in CS is greater than would be expected if mononuclear [Pd(OH)<sub>4</sub>]<sup>2-</sup> complexes were formed. Thus, with  $\chi = 2$  half of the total Pd is in the form of [PdCl<sub>4</sub>]<sup>2-</sup> in solution, and the other half is contained in PHC in accordance with Eq.(2). If only mononuclear complexes [Pd(OH)<sub>4</sub>]<sup>2-</sup> are assumed to be formed, and C<sub>Pd</sub> = 0.2, there should be

$$\delta = \delta_{[PdCl]_{d}} \cdot 0.5C_{Pd} + \delta_{[Pd(OH)]_{d}} \cdot 0.5C_{Pd} + \delta_{[Cl]} \cdot 2C_{Pd} = 21,$$

while  $\delta = 35$  was observed in the experiments.

The difference seems to result from the interaction of  $Cs^+$  and PHC. In this case the peak broadening in the <sup>133</sup>Cs NMR spectrum (Fig. 5, curve *I*) can be related both to a increase in viscosity and to this interaction.





**Fig. 5.** Peak widths in the <sup>133</sup>Cs NMR spectra versus  $\chi$  ( $C_{Pd} = 0.2 M$ ,  $C_{Cs} = 0.07 M$ ) of the solutions without supporting electrolyte (I) and those with  $C_{NaCl} = 2 M$  (2).

At  $\chi = 1.2$  a sharp shift and peak broadening are accompanied by the appearance of another narrower line in the <sup>133</sup>Cs NMR spectrum (Fig. 4, curve 3). The position of the narrow peak corresponds to the <sup>133</sup>Cs chemical shift in the solution containing 0.05 *M* Na<sub>2</sub>PdCl<sub>4</sub> and 0.6 *M* NaCl. There is almost no interaction between these cesium ions and PHC. Some broadening (compared to Na<sub>2</sub>PdCl<sub>4</sub> solutions) of the narrow peak can occur due to the high viscosity of the solution: gel formation is observed at C<sub>Pd</sub> = 0.2 and  $\chi = 1.4$ .

One broad peak in the spectrum corresponds to cesium ions reacting with PHC. As a result of coagulation of primary PHC particles, a portion of the Cs<sup>+</sup> ions is assumed to appear in the closed cells built of PHC chains and, thus, is isolated from the bulk solution (a broad peak in the <sup>133</sup>Cs NMR spectrum). Another portion of the Cs<sup>+</sup> ions is located outside the PHC and reacts with H<sub>2</sub>O, Cl<sup>-</sup>, [PdCl<sub>4</sub>]<sup>2-</sup>.

No dramatic changes in CS and peak widths in the <sup>133</sup>Cs NMR spectrum, as in the previous case, were observed upon titration of Na<sub>2</sub>PdCl<sub>4</sub> in 2 *M* NaCl (Fig. 4 and 5, curves 2). At  $\chi = 1.2$  the CS drops to a value close to that of Cs<sup>+</sup> in the corresponding NaCl solution. The absence of a broad peak like that observed in solutions without the supporting electrolyte can be related to the fact that the possible coordination sites of Cs<sup>+</sup> in PHC are already occupied by Na<sup>+</sup> ions.

Similar phenomena were also observed in the <sup>23</sup>Na NMR. Figure 6 shows changes in the peak width of the <sup>23</sup>Na NMR spectrum during Na<sub>2</sub>PdCl<sub>4</sub> titration by a KOH solution. A  $\Delta f$  increase near  $\chi = 1.2$  is seen on the

Fig. 6. Peak widths in the <sup>23</sup>Na NMR spectra versus  $\chi$  ( $C_{\rm Pd} = 0.2 M$ ).

plot which demonstrates similarity in the behavior of Na<sup>+</sup> and Cs<sup>+</sup>. Due to the poor sensitivity of the CS in  $^{23}$ Na NMR to variations in the medium components, there were no changes in CS during the titration.

The Na<sup>+</sup> concentration in the solution with  $\chi = 2$  (a precipitate was filtered off) was estimated by <sup>23</sup>Na NMR, and *ca.* 1 Na<sup>+</sup> ion per palladium atom was shown to remain in the precipitate. Alkali metal ions behave supposedly as «cross-linking» sites of polymeric chains of palladium hydroxide molecules and thus participate in the formation of colloidal products of alkaline hydrolysis of Pd(II).

Taking into account the cationic and anionic mass balance, alkaline hydrolysis of palladium (II) compounds can be formulated as follows:

(a)  $\operatorname{Na_2PdCl_4} + 2\operatorname{NaOH} \rightarrow \operatorname{Na_2[Pd(OH)_2Cl_2]} + 2\operatorname{NaCI}$ , (b)  $n\operatorname{Na_2[Pd(OH)_2Cl_2]} \rightarrow {\operatorname{Na_n[Pd(OH)_2]_n}} \cdot n\operatorname{CI} + n\operatorname{NaCI}$ .

Because of the fast stage (b), the products of stage (a) could not be detected.

The combined body of results obtained by UV and NMR spectroscopy allows one to assume that PHC possess an extended thread-like structure «wrapped» into a compact particle due to interaction with alkali metal cations. The enlargement of PHC particles appears to take place during coagulation, when the excessive cations are transferred to the «external» (with respect to PHC) solution. Cl-ions are not directly involved in PHC, but, as a component of the double electric layer, they can participate in the formation of colloidal PHC particles.

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