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INTERACTION OF PALLADIUM(II) WITH ALKYLENEDIAMINETETRA(METHYLENEPHOSPHONIC) ACIDS.

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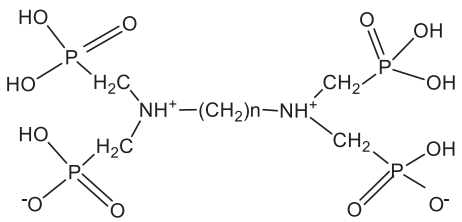
The interaction of K_2PdCl_4 with ethylenediaminetetra(methylenephosphonic) (edtmp, H_8L^1) and pentamethylenediaminetetra(methylenephosphonic) (pendtmp, H_8L^2) acids in solutions with physiological chloride ion concentration (0.15 mol L^{-1} KCl) was studied by pH-potentiometry, UV-Vis and NMR spectroscopy. It was established that in the Pd(II)-edtmp and Pd(II)-pendtmp systems at a metal-ligand ratio of 1:1, complexes of equimolar composition $[Pd(H_4L^{1,2})Cl_2]^{4-}$, $[Pd(H_3L^{1,2})Cl]^{4-}$, $[Pd(H_2L^{1,2})Cl]^{5-}$, $[Pd(HL^{1,2})Cl]^{6-}$, and $[Pd(L^{1,2})Cl]^{7-}$ are formed, for which formation constants were calculated, and distribution diagrams of equilibrium concentrations were constructed as a function of solution pH. A bidentate mode of coordination of edtmp and pendtmp to the central metal ion by the nitrogen and oxygen atoms of the phosphonate group in the $[Pd(H_4L^{1,2})Cl_2]^{4-}$ complex and a tridentate mode by a nitrogen atom and two oxygen atoms of two phosphonate groups of one aminodi(methylphosphonate) moiety of ligands in complexes of the compositions $[Pd(H_3L^{1,2})Cl]^{4-}$, $[Pd(H_2L^{1,2})Cl]^{5-}$, $[Pd(HL^{1,2})Cl]^{6-}$, and $[Pd(L^{1,2})Cl]^{7-}$ were determined. At the concentration ratio Pd(II)-edtmp=2:1 at pH>3, sparingly soluble hydrolysis products were formed in solutions, indicating the absence of interaction between the non-coordinated aminodi(methylphosphonate) moiety of the ligand and Pd(II) to form a binuclear complex. In contrast to edtmp, the system $K_2[PdCl_4]$-pendtmp at a 2:1 ratio exhibited the formation of binuclear complexes $[Pd_2(H_3L^2)Cl_4]^{5-}$, $[Pd_2(H_2L^2)Cl_2]^{4-}$, $[Pd_2(HL^2)Cl_2]^{5-}$, and $[Pd_2(L^2)Cl_2]^{6-}$. In the $[Pd_2(H_3L^2)Cl_4]^{5-}$ complex, two aminodi(methylphosphonate) moieties of pendtmp are coordinated to two Pd(II) ions in a bidentate mode by nitrogen and oxygen atoms of the phosphonate group, and in the complexes $[Pd_2(H_2L^2)Cl_2]^{4-}$, $[Pd_2(HL^2)Cl_2]^{5-}$, and $[Pd_2(L^2)Cl_2]^{6-}$, they are coordinated in a tridentate mode by a nitrogen atom and two oxygen atoms of two phosphonate groups.

Keywords: aminopolyphosphonates, palladium complexes, formation constants.

INTRODUCTION. The synthesis and investigation of complex compounds of metal ions with aminopolyphosphonates (APPs) are of significant interest due to their wide application in industry, agriculture, and medicine. The medical application of this class of compounds is based on their affinity to the bone matrix, which determines the ability of phosphonate-containing compounds to accumulate in the sites of bone tissue lesion caused by malignant tumors or metastases [1, 2]. Stable complexes of ethylenediaminetetra(methylenephosphonic) acid (edtmp) with radionuclides ^{153}Sm, ^{166}Ho, ^{177}Lu, and ^{90}Y have been synthesized as therapeutic agents for the diagnosis and palliative treatment of patients with bone lesions [3, 4]. This has led to numerous studies on the complex formation of APPs with a range of lanthanides, alkaline earth metals, and 3d-metals, which involved determining the stability of the formed complexes, the composition of their inner coordination sphere, and the mode of ligand coordination to the metal ion.

The combination of platinum-group metals with APPs in a complex offers the potential for directed delivery of cytotoxic agents to bone lesions, offering a promising avenue for the creation of potent anti-tumor treatments. Notably, among the platinum group metals, palladium(II) compounds demonstrate cytotoxic effects comparable to platinum compounds but with markedly reduced toxicity [5]. In review articles on chemotherapeutic agents based on Pd(II) complexes with bulky aromatic or aliphatic nitrogen- and sulfur-containing ligands, the importance of the strategy for developing anticancer drugs based on them is emphasized [6, 7].

In the previous article, the results of the study of the acid-base properties of ethylenediaminetetra(methylenephosphonic) acid (edtmp, H_8L^1) and pentamethylenediaminetetra(methylenephosphonic) acid (pendtmp, H_8L^2) were presented [8]. The presence of four acidic PO_3^{2-} groups and two basic nitrogen atoms in the molecules of edtmp and pendtmp determines diverse possibilities for their coordination to Pd(II), formation both of complexes with ligand anions with different degrees of protonation, and binuclear complexes.



n=2 (edtmp), 5 (pendtmp)

In this work we have studied reactions of Pd(II) with edtmp and pendtmp acids in solutions with chloride ion concentration (0.15 mol L^{-1}) at Pd(II):ligand ratios of 1:1 and 2:1.

EXPERIMENT AND DISCUSSIONS OF THE RESULTS. N,N,N',N'-ethylenediaminetetra(methylenephosphonic) acid hydrate, obtained from 'abcr' Germany, and N,N,N',N'-pentamethylenediaminetetra(methylenephosphonic) acid (pendtmp) synthesized *via* a modified Kabachnik-Fields reaction [8] were used in the work. The starting salt K_2PdCl_4 was prepared as described in [9].

All the experiments were accomplished in aqueous solution at a constant temperature of 20.0 ± 0.1 ˚C in a temperature-controlled vessel and constant concentrations of KCl (0.15 mol L^{-1}). The pH measurements of solutions were performed using a 827 pH lab meter (Metrohm). Standard buffer solutions with pH 1.68, 6.86, and 9.18 were used for pH meter calibration. The spectrophotometric studies

were conducted for a series of solutions with metal:ligand ratios of 1:1 and 2:1 at Pd(II) concentrations of $2.5 \cdot 10^{-3}$ mol L^{-1} and $5 \cdot 10^{-3}$ mol L^{-1}. The electronic absorption spectra (EAS) were recorded using a Specord-M40 spectrophotometer in a quartz cuvette (l=0.2 cm and 1 cm). The nuclear magnetic resonance (NMR) spectra (^{31}P-{H}) were recorded on a Bruker AVANCE 400 spectrometer without deuterium stabilization of the resonance conditions. ^{31}P NMR chemical shifts values were determined relative to external 85% H_3PO_4. The pH measurements, recording of EASs, and NMR spectra were conducted 24 hours after the preparation of a series of solutions containing palladium(II) and ligand.

The formation constants of complexes were calculated using the PSEQUAD program [10] based on pH-potentiometry and spectrophotometry data of two parallel series from the formula: $\beta=[M_xL_yH_zCl_q]/[M]^x[L]^y[H]^z[Cl]^q$ and using formation constants of protonated forms of the alkylendiaminetetra(methylenephosphonic) acids understudy. The composition of the inner coordination sphere (chromophore) of the palladium(II) complexes was determined by comparing the positions of the absorption band maxima in the EASs ($\nu_{exp.}$) with the position of the maximum calculated by formula (1):

$$\nu_{calc.}=n1\nu(Cl)+n2\nu(O_{aqua})+ +n3\nu(N_{amin.})+n4\nu(O_{phosphon.}) \quad (1),$$

where n_i is the number of donor atoms of each type; ν is the increment value for a donor atom of each type (cm^{-1}): ν(Cl) = 5170, $\nu(O_{aqua})$ = 6580, $\nu(N_{amin.})$ = 8460 and $\nu(O_{phosphon.})$ = 6831 [11, 12].

The interaction of K_2PdCl_4 with edtmp.

The electronic absorption spectra (EASs) of solutions of the K_2PdCl_4-edtmp=1:1 system upon addition of 1 to 8 equivalents of base in the pH range of 1.92–9.21 are shown in Figure 1.

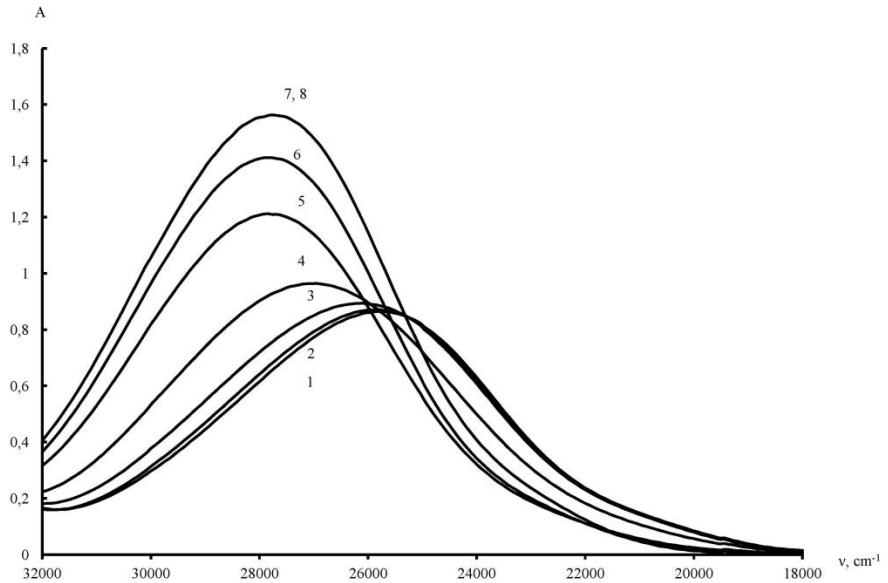
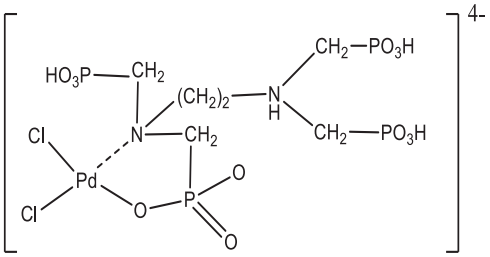


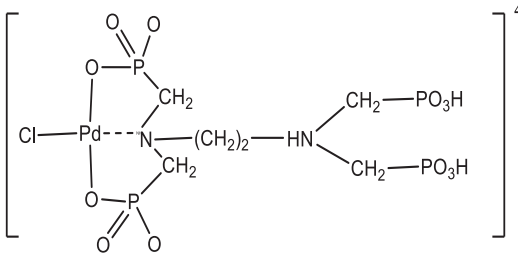
Fig. 1. EASs of the K_2PdCl_4-edtmp=1:1 system ($C_{Pd(II)}=C_{edtmp}=5 \cdot 10^{-3}$ mol L^{-1}, C_{KCl}=0.15 mol L^{-1}, pH: 1.92 (1); 2.13 (2); 2.53 (3); 3.28 (4);4.40 (5); 6.41 (6); 7.21 (7); 9.21 (8)).

The position of the absorption band maximum in the EASs of solutions with pH 1.92 and 2.13 at 25800 cm^{-1} indicates the formation of a complex with the chromophore composition [Pd;$N_{amin.}$; $O_{phosphon.}$; 2Cl] ($\nu_{calc.}$=25600 cm^{-1}). In this complex, the ligand is bidentately coordinated to Pd(II) by the nitrogen and oxygen atoms of the phosphonate group. The formation constant of this complex was determined from spectrophotometry and pH-potentiometry data of solutions with constant concentration of K_2PdCl_4 and concentration of edtmp varying to the metal-to-ligand ratio of 1:1 (see Table 1).

The shift of the absorption band maximum to 27600 cm^{-1} upon pH increase to 4.40 can be explained by the formation of a complex with chromophore of the composition [Pd; Namin.; 2Ophosphon.; Cl] ($\nu_{calc.}$=27300 cm^{-1}), where edtmp coordinates to Pd(II) in a tridentate manner through a nitrogen atom and two oxygen atoms of the phosphonate groups of one aminodi(methylenephosphonate) moiety.



$[Pd(H_4L^1)Cl_2]^{4-}$



$[Pd(H_3L^1)Cl]^{4-}$

Table 1.

Calculated formation constants of complexes of Pd(II) with edtmp and pendtmp.

The composition of complexes*	lgβ
$[Pd(H_4L^1)Cl_2]^{4-}$	52.41 (9)
$[Pd(H_3L^1)Cl]^{4-}$	47.84 (9)
$[Pd(H_2L^1)Cl]^{5-}$	41.60 (8)
$[Pd(HL^1)Cl]^{6-}$	34.24 (6)
$[Pd(L^1)Cl]^{7-}$	26.40 (7)
$\{Pd(H_2L^2)Cl_2\}$	37.20 (6)
$\{Pd(HL^2)Cl\}$	31.31 (4)
$\{Pd(L^2)Cl\}$	23.60 (5)
$\{Pd_2(HL^2)Cl_2\}$	46.17 (9)
$\{Pd_2LCl_2\}$	41.87 (8)
$\{Pd_2LH_{-1}\}$	34.60 (8)
$\{Pd_2LH_{-2}\}$	25.32 (8)

* - in [ ] is given the actual composition of complexes, and in { } the conditional composition of complexes.

The invariable position of the absorption maximum at 27600 cm^{-1} in the EASs at pH 4.40 – 9.11 indicates the formation of a number of complexes with the same chromophore upon sequential deprotonation of the coordinated ligand.

The calculated formation constants of Pd(II) complexes with edtmp were used to construct distribution diagrams of their equilibrium concentrations as a function of pH (Fig. 2).

As evident from the diagram, complex formation in the system $K_2[PdCl_4]$–edtmp occurs already in strongly acidic conditions at pH<2. At physiological pH values, the dominant complexes are $[Pd(H_2L^1)Cl]^{5-}$ and $[Pd(HL^1)Cl]^{6-}$.

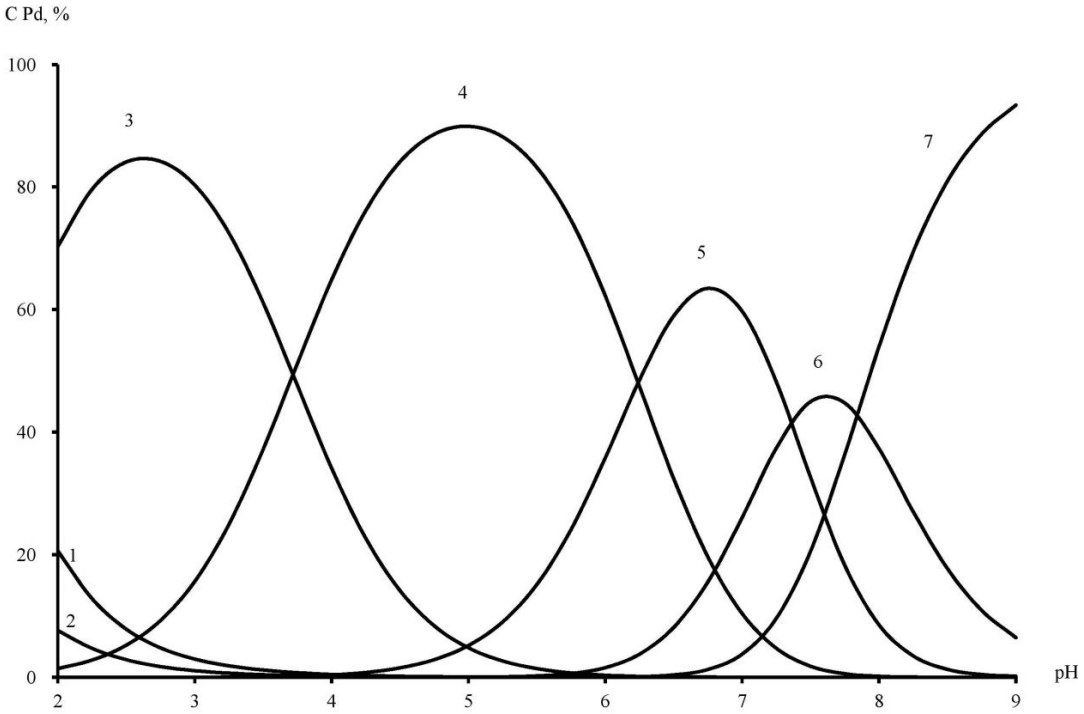


Fig. 2. Equilibrium concentration distribution diagram for the complexes formed in the K_2PdCl_4–edtmp=1:1 system (C_{KCl}=0.15 mol L^{-1}; $[PdCl_4]^{2-}$ (1); $[PdCl_3]^-$ (2); $[Pd(H_4L^1)Cl_2]^{4-}$ (3); $[Pd(H_3L^1)Cl]^{4-}$ (4); $[Pd(H_2L^1)Cl]^{5-}$ (5); $[Pd(HL^1)Cl]^{6-}$ (6); $[Pd(L^1)Cl]^{7-}$ (7)).

To investigate the potential formation of a binuclear complex upon binding by excess Pd(II) the free aminodi(methylenephosphonate) moiety of edtmp, complexation reactions were studied in the system $K_2[PdCl_4]$–edtmp=2:1. In solutions of this system under the conditions of double excess of Pd(II) at pH>3, the formation of sparingly soluble hydrolysis products was observed, indicating the absence of interaction between the free aminodi(methylenephosphonate) moiety of the ligand and excess Pd(II) to form a binuclear complex. In this case, the absence of binuclear complex formation can be explained by steric hindrances.

The proposed scheme of complex formation in the K_2PdCl_4–edtmp=1:1 system was confirmed by ^{31}P NMR spectroscopy data (Fig. 3).

In the ^{31}P NMR spectra of solutions in the pH range of 1.92 to 3.28, three signals of phosphorus nuclei were observed. The signals at δP~41.0 ppm and δP~8.8 ppm, which exhibit equal integral intensities, correspond to the coordinated and free phosphonate groups of one aminodi(methylenephosphonate) moiety in the complex $[Pd(H_4L^1)Cl_2]^{4-}$. The signal of phosphorus nuclei at δP~10.5 ppm, whose integral intensity is twice as high, corresponds to the two phosphonate groups of the free aminodi(methylenephosphonate) moiety of the ligand. In the ^{31}P NMR spectra of solutions with pH>4.40, two signals of phosphorus nuclei with equal integral intensities were observed upon the formation of complexes with edtmp tridentately coordinated to the central metal

ion. The signal at δP~33.9 ppm corresponds to the two coordinated phosphonate groups of the one aminodi(methylphosphonate) moiety, while the signal at δP~7.6 ppm corresponds to non-coordinated phosphonate groups of another aminodi(methylphosphonate) moiety of the ligand. Thus, the sequence of complex formation in the system $K_2[PdCl_4]$–edtmp=1:1, as depicted by the equilibrium concentration distribution diagram for complexes (Fig. 2), is consistent with the ^{31}P NMR spectroscopy data.

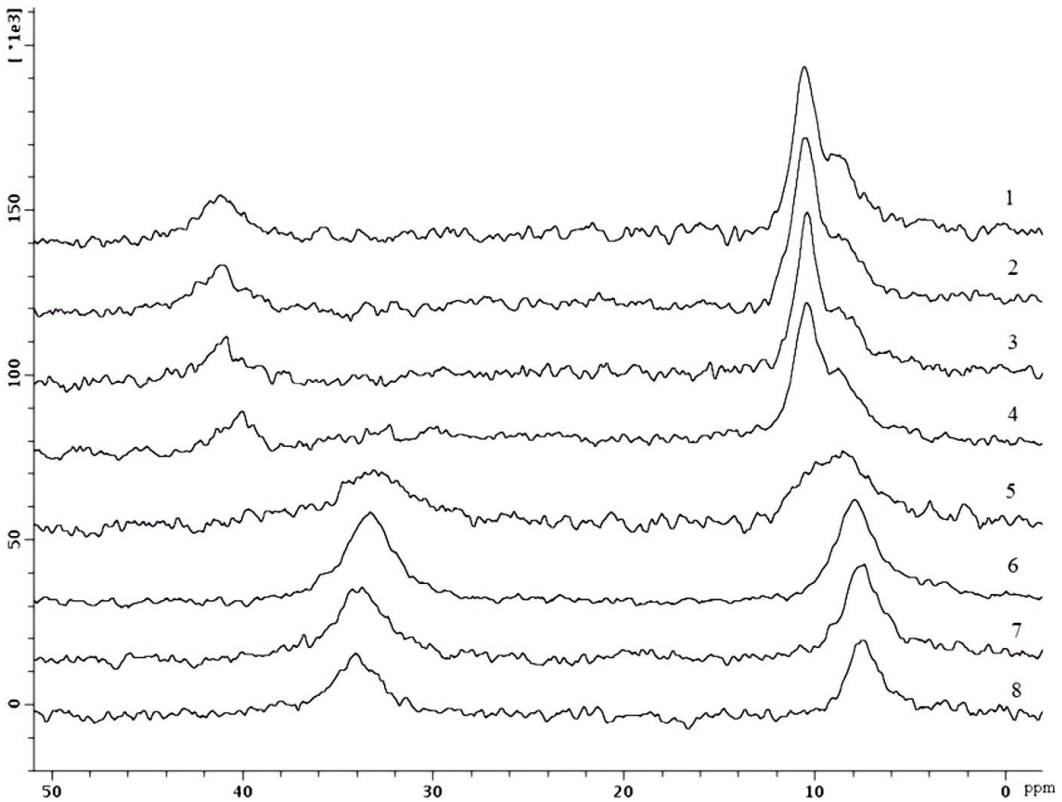


Fig. 3. ^{31}P-{H} NMR spectra of the K_2PdCl_4–edtmp=1:1 system ($C_{Pd(II)}=C_{edtmp}=5\cdot10^{-3}$ mol L^{-1}, pH: 1.92 (1); 2.13 (2); 2.53 (3); 3.28 (4); 4.40 (5); 6.41 (6); 7.21 (7); 9.21 (8)).

Interaction of K_2PdCl_4 with pendtmp.

In the EASs of the $K_2[PdCl_4]$–pendtmp=1:1 system upon pH increase from 2.50 to 4.10, a shift of the absorption band with a maximum at 21600 cm^{-1}, corresponding to a mixture of $[PdCl_4]^{2-}$ and $[PdCl_3H_2O]^-$, to 25600 cm^{-1} was observed, indicating the formation of a complex with chromophore of the composition [Pd; $N_{amin.}$; $O_{phosphon.}$; 2Cl] (Fig. 4a). Further shift of the absorption band maximum to 26900 cm^{-1}, observed upon pH change from 4.99 to 7.73, corresponds to the formation of complexes with the same chromophore composition [Pd; N_{amin}.; $2O_{phosphon.}$; Cl].

In the pH range of 2.51 to 8.46 of the aqueous solutions of the $K_2[PdCl_4]$–pendtmp=2:1 system, changes in the absorption band position similar to those observed in the

$K_2[PdCl_4]$–pendtmp=1:1 system were recorded with nearly a twofold increase in the intensity of the absorption bands with maxima at 25600 cm^{-1} and 26900 cm^{-1}, respectively (Fig. 4b). This suggests the formation in this system of binuclear complexes with the coordination of two Pd(II) ions to the two aminodi(methylenephosphonate) moieties of pendtmp. Thus, binuclear complexes contain two chromophoric groups each: [Pd; $N_{amin.}$; $O_{phosphon.}$; 2Cl] or [Pd; $N_{amin.}$; $2O_{phosphon.}$; Cl].

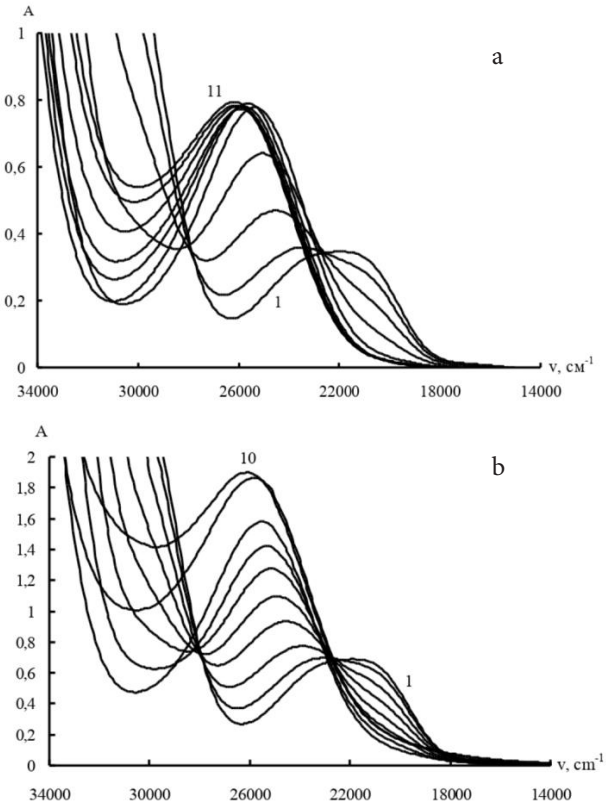


Fig. 4. EASs of the K_2PdCl_4-pendtmp system ((a) $C_{Pd(II)}=C_{pendtmp}=2.5\cdot10^{-3}$ mol L^{-1}, $C_{KCl}=0.15$ mol L^{-1}, pH: 2.50 (1); 2.88 (2); 3.22 (3); 3.57 (4);4.10 (5); 4.99 (6); 5.68 (7); 6.41 (8); 7.27 (9); 7.66 (10); 7.73 (11), (b) $C_{Pd(II)}=5\cdot10^{-3}$ mol L^{-1}, $C_{pendtmp}=2.5\cdot10^{-3}$ mol L^{-1}, pH: 2.51 (1); 2.81 (2); 3.09 (3); 3.36 (4);3.61 (5); 3.81 (6); 4.35 (7); 5.43 (8); 7.93 (9); 8.46 (10)).

In Table 1, the conditional composition of Pd(II) complexes with pendtmp is presented, for which formation constants were calculated considering the formation constants of the protonated forms of pendtmp as for a conditionally pentadentate acid [8].

Diagrams of equilibrium concentration distribution of complexes as a function of pH were constructed, based on calculated formation constants of Pd(II) complexes with pendtmp, for the systems K_2PdCl_4-pendtmp=1:1 and 1:2, which show the conditional and real compositions of complexes (Fig. 5).

It is seen from Fig. 5 that complex formation in the K_2PdCl_4-pendtmp=1:1 system begins at pH~3, which is higher than the corresponding pH value for the $K_2[PdCl_4]$-edtmp=1:1 system. It should be noted that at the same pH values, the composition of equimolar Pd(II) complexes with pendtmp contains ligand forms with higher degree of protonation than in the case of equimolar complexes of Pd(II) with edtmp. Formation of equimolar and binuclear complexes in the $K_2[PdCl_4]$-pendtmp system is confirmed by ^{31}P NMR spectroscopy data.

In the ^{31}P NMR spectra of solutions of the system $K_2[PdCl_4]$–pendtmp=1:1, the redistribution of integral intensity between the signals of phosphorus nuclei of free phosphonate groups with δP~7.7 ppm and the signals of the coordinated phosphonate groups with δP~36.5 ppm and δP~33.4 ppm upon pH increase from 2.95 to 3.97 may indicate the formation of complexes of the equimolar composition $[Pd(H_4L^2)Cl_2]^{4-}$ with the chromophore [Pd; $N_{amin.}$; $O_{phosphon.}$; 2Cl] and $[Pd(H_3L^2)Cl]^{4-}$ with the chromophore [Pd; $N_{amin.}$; $2O_{phosphon.}$; Cl] (Fig. 6a). The presence of two signals of phosphorus nuclei of coordinated phosphonate groups in a downfield region, each of which is a superposition of

several signals, may be due to the presence of several conformational states of the ligand in the coordination sphere of the complexes [13]. Upon further increase in pH, deprotonation of the coordinated ligand occurs without change in the donor composition of the coordination sphere of the complexes.

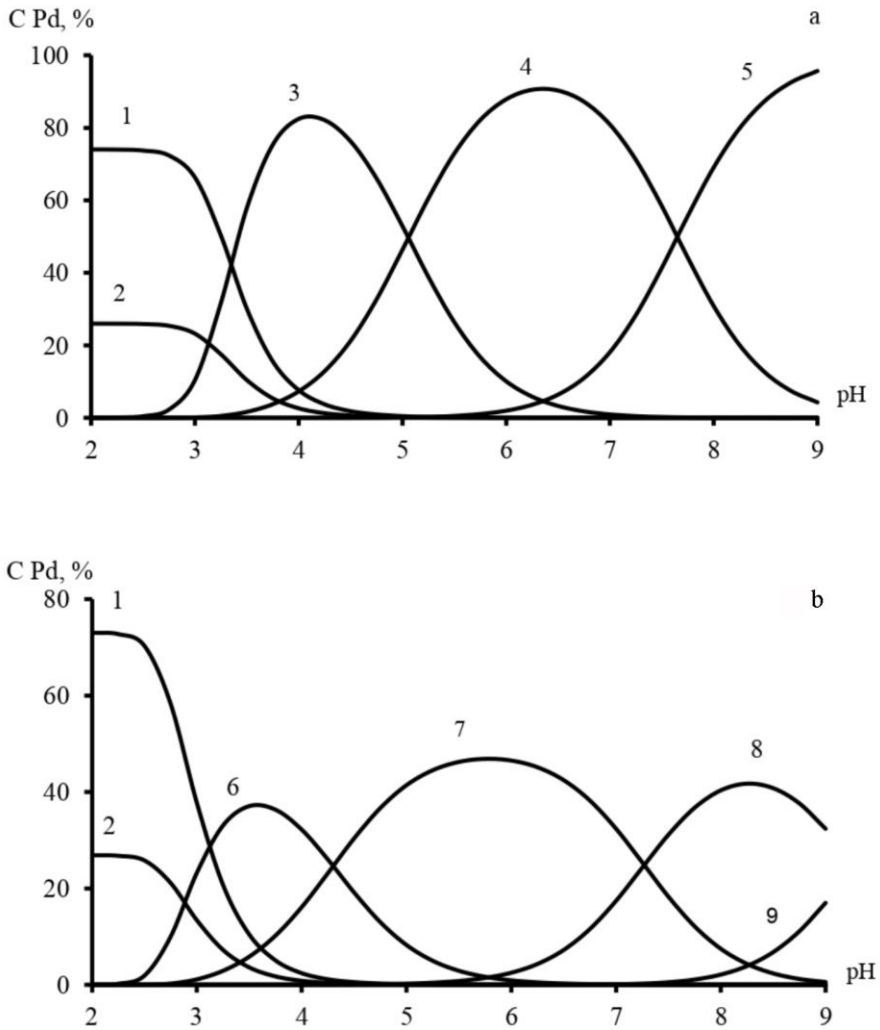


Fig. 5. Equilibrium concentration distribution diagrams complexes in the K_2PdCl_4–pendtmp systems*
((a) $K_2[PdCl_4]$–pendtmp=1:1, (b) $K_2[PdCl_4]$–pendtmp=2:1. ($[PdCl_4]^{2-}$ (1); $[PdCl_3]^-$ (2); $\{Pd(H_2L^2)Cl_2\}$ $[Pd(H_4L^2)Cl_2]^{4-}$ (3); $\{Pd(HL^2)\}$ $[Pd(H_3L^2)Cl]^{4-}$ (4); $\{Pd(L^2)\}$ $[Pd(H_2L^2)Cl]^{5-}$ (5); $\{Pd_2(HL^2)Cl_4\}$ $[Pd_2(H_3L^2)Cl_4]^{5-}$ (6); $\{Pd_2(L^2)Cl_2\}$ $[Pd_2(H_2L^2)Cl_2]^{4-}$ (7); $\{Pd_2(H_{-1}L^2)Cl_2)$ $[Pd_2(HL^2)Cl_2]^{5-}$ (8); $\{Pd_2(H_{-2}L^2)Cl_2\}$ $[Pd_2(L)Cl_2]^{6-}$ (9)).
*- in [ ] is given the actual composition of complexes and in { } the conditional composition of complexes.

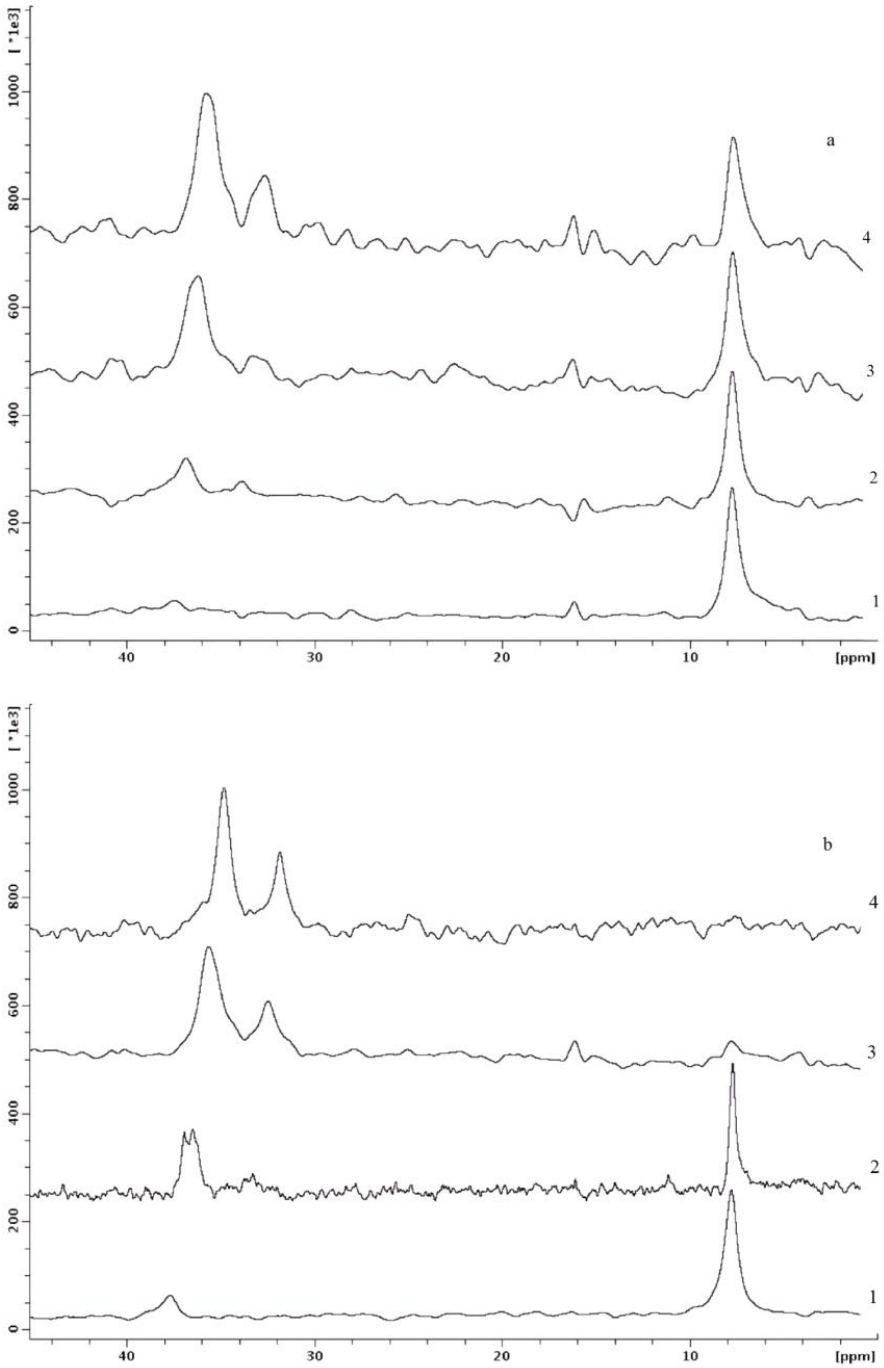
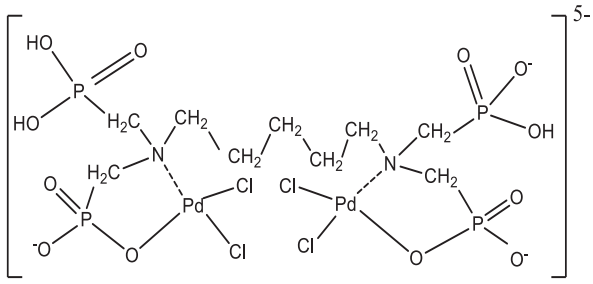
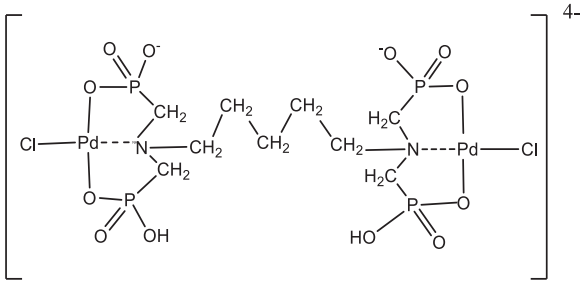


Fig. 6. ^{31}P-{H} NMR spectra of the $K_2[PdCl_4]$–pendtmp systems ((a) $C_{Pd(II)}=C_{pendtmp}=2\cdot10^{-3}$ mol L^{-1}, pH: 2.95 (1); 3.27 (2); 3.61 (3); 3.97 (4). (b) $C_{Pd(II)}=4\cdot10^{-3}$ mol L^{-1}, $C_{pendtmp}=2\cdot10^{-3}$ mol L^{-1}, pH: 2.28 (1); 3.42 (2); 4.11 (3); 4.69 (4)).

As can be seen from the ^{31}P NMR spectra of solutions of the $K_2[PdCl_4]$–pendtmp=2:1 system in the pH range of 2.28–3.42, in the down field region there are signals of phosphorus nuclei that correspond to phosphonate groups coordinated to Pd(II), and in the upfield region to the free phosphonate groups of the ligand (Fig. 6b). The presence of signals from phosphorus nuclei in coordinated phosphonate groups (δP~36.5 ppm and δP~33.4 ppm) and the absence of signals of phosphorus nuclei of free phosphonate groups at pH>4.11 indicate the formation of binuclear complexes with the coordination of two aminodi(methylenephosphonate) moieties of the ligand to two Pd(II) ions, the donor environment of each of which has the composition [Pd; $N_{amin.}$; $2O_{phosphon.}$; Cl].



$[Pd_2(H_3L^2)Cl_4]^{5-}$



$[Pd_2(H_2L^2)Cl_2]^{4-}$

Binuclear Pd(II) complexes with pendtmp exist in solution as several conformers, as evidenced by the presence in the ^{31}P NMR spectra of two signals of the phosphorus nuclei of coordinated phosphonate groups in a down field region.

CONCLUSIONS. The results of the study have shown that in the systems $K_2[PdCl_4]$-edtmp=1:1 and $K_2[PdCl_4]$-pendtmp=1:1, complexes of equimolar composition $[Pd(H_4L^{1,2})Cl_2]^{4-}$, $[Pd(H_3L^{1,2})Cl]^{4-}$, $[Pd(H_2L^{1,2})Cl]^{5-}$, $[Pd(HL^{1,2})Cl]^{6-}$, and $[Pd(L^{1,2})Cl]^{7-}$ are formed. Electron and ^{31}P NMR spectroscopic data indicate the bidentate mode of coordination of edtmp and pendtmp to the central metal ion *via* the nitrogen and oxygen atoms of the phosphonate group in the complex $[Pd(H_4L^{1,2})Cl_2]^{4-}$ and a tridentate coordination of ligands by a nitrogen atom and two oxygen atoms of two phosphonate groups of one aminodi(methylenephosphonate) moiety in the complexes $[Pd(H_3L^{1,2})Cl]^{4-}$, $[Pd(H_2L^{1,2})Cl]^{5-}$, $[Pd(HL^{1,2})Cl]^{6-}$, and $[Pd(L^{1,2})Cl]^{7-}$. At a metal concentration ratio of 2:1 in the case of edtmp, the formation of sparingly soluble hydrolysis products was observed in solutions, indicating the impossibility of formation of a binuclear complex with the coordination of the second aminodi(methylenephosphonate) moiety of edtmp by excess Pd(II).

In contrast to edtmp, in the system $K_2[PdCl_4]$-pendtmp=2:1, the formation of binuclear complexes $[Pd_2(H_3L^2)Cl_4]^{5-}$, $[Pd_2(H_2L^2)Cl_2]^{4-}$, $[Pd_2(HL^2)Cl_2]^{5-}$, and $[Pd_2(L^2)Cl_2]^{6-}$ was established. In the complex $[Pd_2(H_3L^2)Cl_4]^{5-}$, two aminodi(methylenephosphonate) moieties of pendtmp coordinate bidentately to two Pd(II) ions *via* the nitrogen and oxygen atoms of the phosphonate group. In the complexes $[Pd_2(H_2L^2)Cl_2]^{4-}$, $[Pd_2(HL^2)Cl_2]^{5-}$, and

$[Pd_2(L^2)Cl_2]^{6-}$, two aminodi(methylphosphonate) moieties of pendtmp coordinate tridentately to two Pd(II) ions *via* a nitrogen atom and two oxygen atoms of two phosphonate groups. The possibility of formation of binuclear complexes during the interaction of Pd(II) with pendtmp is realized due to the remote location of two aminodi(methylphosphonate) moieties, whereas closely located aminodi(methylphosphonate) moieties, as in the case of edtmp, hinder the coordination of the second aminodi(methylphosphonate) moiety by excess Pd(II) due to steric hindrances.

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ВЗАЄМОДІЯ ПАЛАДІЮ(II) З АЛКІЛЕНДІАМІНТЕТРА(МЕТИЛЕНФОСФОНОВИМИ) КИСЛОТАМИ

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Методами pH-потенціометрії, електронної та ЯМР ^{31}P спектроскопії досліджено комплексоутворення K_2PdCl_4 з етилендіамінтетра(метиленфосфоновою) (edtmp, H_8L^1) та пентаметилендіамінтетра(метиленфосфоновою) (pendtmp, H_8L^2) кислотами в розчинах із фізіологічною концентрацією хлорид іонів (0.15 моль/л KCl). Встановлено, що в системах Pd(II)-edtmp та Pd(II)-pendtmp при співвідношенні метал – ліганд=1:1 утворюються комплекси еквімолярного складу $[Pd(H_4L^{1,2})Cl_2]^{4-}$, $[Pd(H_3L^{1,2})Cl]^{4-}$, $[Pd(H_2L^{1,2})Cl]^{5-}$, $[Pd(HL^{1,2})Cl]^{6-}$ та $[Pd(L^{1,2})Cl]^{7-}$, для яких розраховано константи утворення та побудовані діаграми розподілу рівноважних концентрацій залежно від pH розчину. Визначено бідентатний спосіб координації edtmp та pendtmp до центрального іона металу атомами нітрогену та оксигену фосфонової групи в комплексі $[Pd(H_4L^{1,2})Cl_2]^{4-}$ та тридентатним атомом нітрогену та двома атомами оксигену двох фосфонових груп одного аміноди(метилфосфонового) фрагмента в комплексах складу $[Pd(H_3L^{1,2})Cl]^{4-}$, $[Pd(H_2L^{1,2})Cl]^{5-}$, $[Pd(HL^{1,2})Cl]^{6-}$ та $[Pd(L^{1,2})Cl]^{7-}$. При співвідношенні концентрації Pd(II)-edtmp=2:1 у розчинах спостерігали утворення малорозчинних продуктів гідролізу, що свідчить про неможливість координації другого іона Pd(II) до другого аміноди(метилфосфонового) фрагмента ліганду та утворення біядерного

комплексу. На відміну від edtmp в системі $K_2[PdCl_4]$-pendtmp=2:1 встановлено утворення біядерних комплексів $[Pd_2(H_3L^2)Cl_4]^{5-}$, $[Pd_2(H_2L^2)Cl_2]^{4-}$, $[Pd_2(HL^2)Cl_2]^{5-}$ та $[Pd_2(L^2)Cl_2]^{6-}$. В комплексі $[Pd_2(H_3L^2)Cl_4]^{5-}$ два аміноди(метилфосфонових) фрагменти pendtmp координовані до двох іонів Pd(II) бідентатно атомами нітрогену та оксигену фосфонової групи, а в комплексах $[Pd_2(H_2L^2)Cl_2]^{4-}$, $[Pd_2(HL^2)Cl_2]^{5-}$ та $[Pd_2(L^2)Cl_2]^{6-}$ – триденттатно атомом нітрогену та двома атомами оксигену двох фосфонових груп.

Ключові слова: амінополіфосфонати, комплекси паладію, константи утворення.

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