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Structure of Palladium(II) Complexes with Nitrilotrimethylenephosphonic Acid in Aqueous Solutions According to ^{31}P and ^{1}H NMR Data

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Abstract—The complex formation in the K_2PdCl_4–nitrilotrimethylenephosphonic acid (NTMP) system with a metal to ligand molar ratio of 1 : 1 and 1 : 2 was studied by ^{31}P and ^{1}H NMR spectroscopy. The formation of equimolar complexes with NTMP coordinated in the bidentate ([N,O]) and tridentate ([N,O,O]) fashions depending on the reactant and chloride ion concentrations and solution pH was observed.

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Aminophosphonic acids and their complexes with various metals find extensive use in medicine, in particular, in treatment of bone tissue diseases [1]. In addition, it was found that some platinum metal complexes with aminophosphonic acids and their derivatives show antitumor activities [2–6]. The composition and structure of platinum(II) and palladium(II) complexes with aminophosphonic acids containing an amino group and one, two, or three phosphonic groups have been studied by ^{1}H, ^{13}C, ^{15}N, ^{31}P, and ^{195}Pt NMR spectroscopy and pH potentiometry [7–10]. It was shown that depending on the structure of aminophosphonic acid, their reactions with palladium(II) and platinum(II) with variation of the reactant ratio and pH give either equimolar or bisligand complexes in which the acid may be coordinated in the monodentate fashion through either nitrogen or oxygen atom, in the bidentate fashion through nitrogen and oxygen atoms, or in the tridentate fashion through nitrogen and two oxygen atoms of the phosphonic groups.

The results of ^{31}P, ^{1}H, and ^{13}C NMR studies of Pt(II) reaction with nitrilotrimethylenephosphonic acid (NTMP, H_6L) show possible formation of square planar complexes with either bidentate ligand coordination through the amine nitrogen atom and the phosphonic oxygen atom or tridentate coordination through the amine nitrogen atom and two oxygen atoms of two phosphonic groups [10]. Data from pH potentiometry and spectrophotometry for the K_2PdCl_4–NTMP system indicated the formation of complex anions $[PdH_3LCl_2]^{3-}$, $[PdH_2LCl_2]^{4-}$, $[PdHLCl_2]^{5-}$, and $[PdLCl_2]^{6-}$, in solutions [11]. The conclusion concerning the [N,O] bidentate coordination of NTMP in these complexes was based on coincidence of experimentally observed ($\nu_{max} = 25300$ cm^{-1}) and empirically calculated ($\nu_{max} = 25500$ cm^{-1}) absorption maxima in the UV/Vis spectra [12]. The calculation was based on the sum of increments of the donor atoms present in the inner coordination sphere of palladium(II) complexes with NTMP, which form the chromophore [Pd; Cl; N_{amine}; $2OPO_3$]. Therefore, it is pertinent to compare the positions of the absorption maxima of palladium(II) complexes with NTMP, nitrilotriacetic acid (NTA), and some aliphatic amino acids, because the increments determining the contributions of oxygens of the carboxyl and phosphonic groups to UV/Vis spectral parameters are similar [12–14]. According to published data [13], the interaction in the $PdCl_2$–NTA system (1 : 1) at pH 3–11 gives rise to equimolar complex with $\nu_{max} = 27800$ cm^{-1}. The NTA coordination mode in the complex was not discussed in the study cited [13]; however, this ν_{max} value suggests a tridentate ligand coordination and formation of a complex with the chromophore [Pd; Cl; N_{amine}; $2O_{carbox}$] for which the calculated $\nu_{max} = 27000$ cm^{-1}. This conclusion is in line with the results of ^{1}H NMR studies of complexation in the $Pd(NO_3)_2$–NTA system [15]. According to increment calculation, the equimolar palladium(II) complex with NTMP coordinated in the tridentate mode and the chromophore [Pd; Cl; N_{amine}; $2OPO_3$] should exhibit an absorption maximum with $\nu_{max} = 27157$cm^{-1}, which is at variance with $\nu_{max} = 25300$ cm^{-1} found experimentally. However, the absorption with $\nu_{max} = 25300$ cm^{-1}

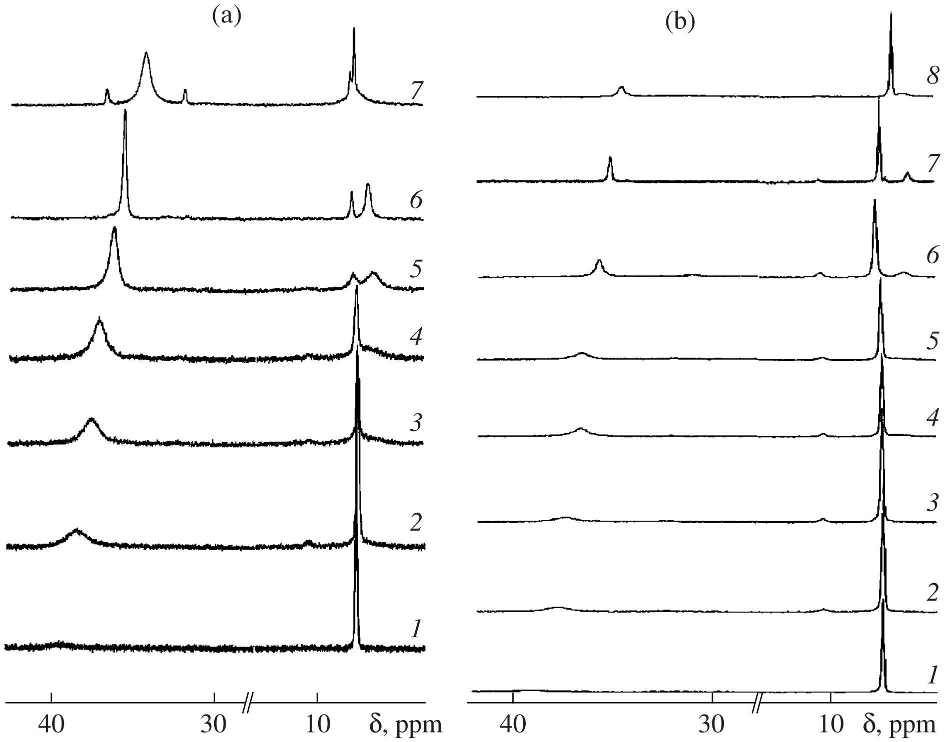


Fig. 1. ^{31}P NMR spectra of the K_2PdCl_4–NTMP system: (a) $c_{K_2PdCl_4} = c_{NTMP} = 0.1$ mol/l, pH = (*1*) 1.80, (*2*) 2.63, (*3*) 3.02, (*4*) 3.24, (*5*) 3.66, (*6*) 6.22, (*7*) 7.50; (b) $c_{K_2PdCl_4} = 0.1$ mol/l, $c_{NTMP} = 0.2$ mol/l, pH = (*1*) 2.28, (*2*) 2.94, (*3*) 3.29, (*4*) 3.44, (*5*) 3.53, (*6*) 4,17, (*7*) 5.20, (*8*) 6.72.

observed in the UV/Vis spectra of solutions of the K_2PdCl_4–NTMP system (1 : 1) corresponds to this characteristics, $\nu_{max} = 25500$ cm^{-1}, for the equimolar complexes formed in the K_2PdCl_4–aliphatic amino acid systems with the chromophore [Pd; 2Cl; N_{amine}; O_{carbox}]. Thus, published data on the structure of the inner coordination sphere of palladium(II) complexes with NTMP are scattered and mainly based on comparison of experimental ν_{max} values with these values calculated empirically.

The purpose of this work was to study systematically the formation and structure of the Pd(II) complexes with NTMP by ^{31}P and ^{1}H NMR spectroscopy and DFT calculations.

EXPERIMENTAL

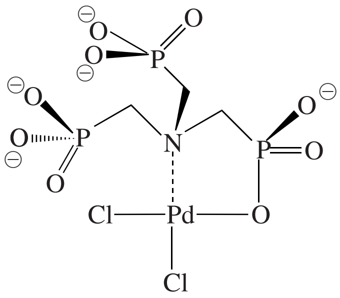
The experimental procedure and conditions for a series of solutions with K_2PdCl_4 : NTMP molar ratios of 1 : 1 and 1 : 2 ($c_{K_2PdCl_4} = 0.1$, $c_{NTMP} = 0.1$ and 0.2 mol/l) are similar to those described previously [16]. The NMR spectra were recorded after equilibrium had been established in solutions.

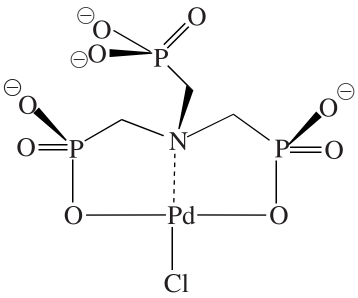
The structures of the studied compounds were optimized within the TURBOMOLE program package in the DFT RI-BP86 approximation using RI (Resolution of the Identity) algorithm [17–20]. The Pd atoms were described using (7*s*6*p*5*d*)/[5*s*3*p*2*d*] basis sets with {31111/411/41} contracting. The inner electron shells of Pd comprising 28 electrons were described by effective pseudopotentials [21]. As the basis sets for other atoms, standard split valence SV(P) basis sets were used [22]: (10*s*7*p*)/[4*s*3*p*] for P with {5311/511} contracting, (7*s*4*p*)/[3*s*2*p*] for C, N, and O with {511/31} contracting, and (4*s*)/[2*s*] for H with {31} contracting. In the description of all atoms of compounds except for hydrogen, one set of *d*-functions was added to the polarization functions. The exponent values included in the basis set by default were used. For optimized structures, vibration frequencies were calculated. The absence of imaginary frequencies attested to the correspondence of the obtained structures to the true local energy minima. The total energy values were corrected taking account the molecular vibrations at 0 K. The optimized structure is presented by means of the VMD program [23].

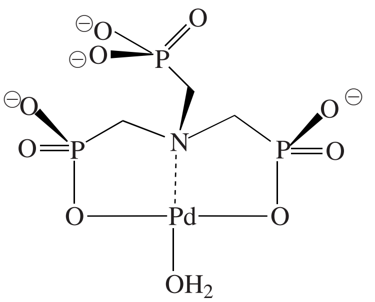
RESULTS AND DISCUSSION

^{31}P NMR for the K_2PdCl_4–NTMP system. The ^{31}P NMR spectrum of aqueous solutions of free NTMP at acidic or neutral pH exhibits a triplet caused by the spin–spin coupling of the phosphorus nuclei with the methylene protons (δ_P = 7.8–6.8 ppm and $^2J_{PH}$ = 12 Hz).

As shown by ^{31}P NMR data (Fig. 1a), an increase in pH from 1.80 to 6.22 in the K_2PdCl_4–NTMP (1 : 1) system causes an increase in the degree of involvement of NTMP functional groups in the formation of Pd(II) coordination sphere. The intensity of the signal with δ_P = 39.4–34.6 ppm corresponding to the coordinated phosphonic groups gradually increases. This is accompanied by a decrease in the intensity of signals of the phosphonic groups not bonded directly to the central atom (δ_P = = 6–8 ppm). The ratio of integral intensities of the coordinated and uncoordinated phosphonic groups equal to 1 : 2 and corresponding to structure **A** is observed at pH 2.63:


(A)


(B)


(C)

As pH increases to ≥7, the second phosphonic group of the ligand may be coordinated to the Pd^{2+} ion with replacement of the chloride ion in the coordination sphere of complex **A**, which gives rise to 2 : 1 ratio of the integral intensities of the signals and to structure **B**. Geometry optimization for structure **A** with total charge of –6 as an isolated anion in the gas-phase approximation results in one Pd–Cl being cleaved during optimization to give an additional P–O–Pd bond (**B**). Quantum chemical calculations show higher stability of a combination of the complex with structure **B** and an isolated chloride anion compared with structure **A**. The theoretically calculated structure of complex **B** with the lowest total energy is shown in Fig. 2.

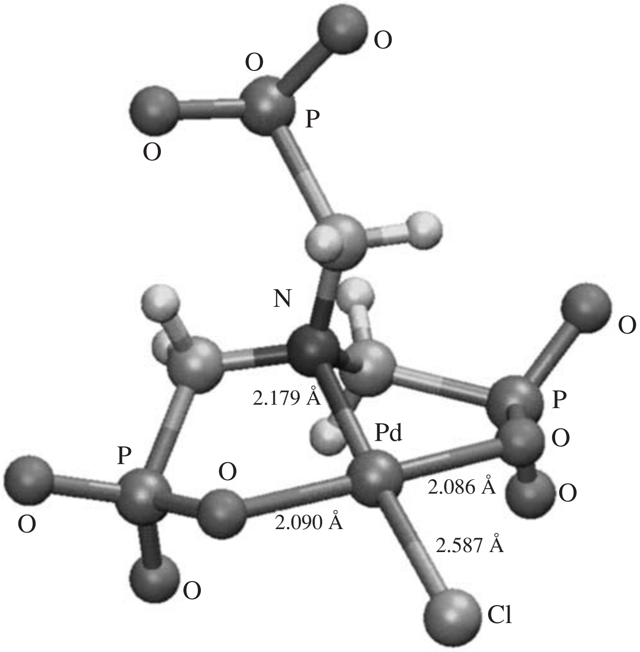


Fig. 2. Optimized (RI-BP86/SV(P)) structure of the complex $[Pd(HTMP)Cl]^{5-}$.

As pH increases, apart from the changes mentioned above, the ^{31}P NMR spectra show also a shift and splitting of the high-field signal corresponding to the phosphonic groups not coordinated to the central atom. This splitting may be indicative of formation of complex associates of the phosphonic groups of neighboring molecules through hydrogen bonds with cations of the bases added to the system and with solvent molecules. The stability and composition of these associates can depend on both the solution pH and the concentration of reactants and determine the changes in the spectral pattern. To elucidate these complexation details, it was important to investigate the evolution of ^{31}P NMR spectra upon variation of the reactant concentration with their equimolar ratio and different pH values: 3.5, 5.0, and 7.4. As can be seen in Fig. 3, upon regular decrease in the reactant concentration with pH being maintained constant, in addition to the signal with δ_P = 36.35–37.17 ppm, the spectrum exhibits a signal with δ_P = 34.3–33.5 ppm; redistribution of the integral intensity between these signals may be indicative of coexistence and interconversion of polynuclear complexes differing in both the degree of association and structural features (linear, cyclic, or branched molecules). Plotting of the dependences $\log c_M - \log I$ (I is the integral intensity of the ^{31}P NMR signals at 36–37 ppm) at pH 3.5, 5.0, and 7.4 demonstrated that for the initial concentrations of 0.1–0.01 mol/l, the degree of association of complexes is close to 5, whereas in the case of concentrations of 0.005–0.001 mol/l, it gradually decreases, the mono-

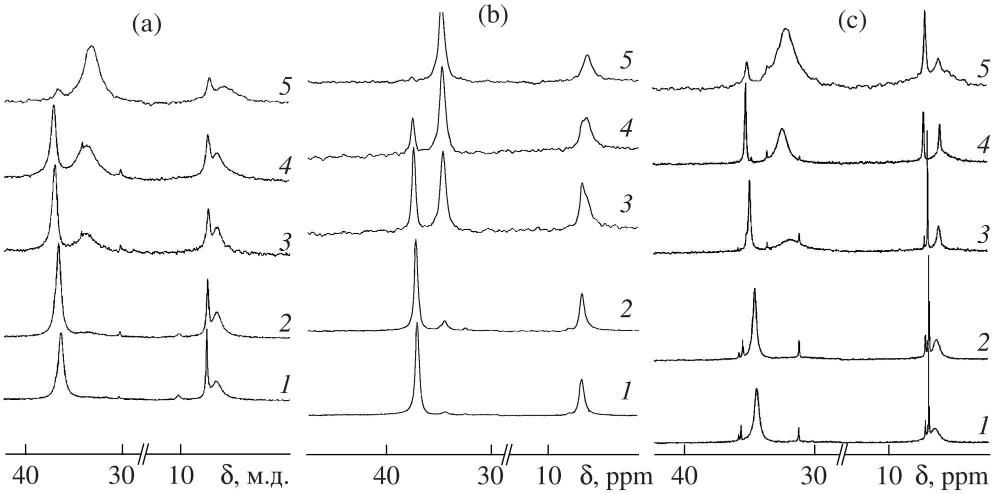


Fig. 3. ^{31}P NMR spectra of the 1 : 1 K_2PdCl_4–NTMP system at $c_{K_2PdCl_4} = c_{NTMP}$: (*1*) 0.1, (*2*) 0.05, (*3*) 0.01, (*4*) 0.005, (*5*) 0.001 mol/l and pH (a) 3.5, (b) 5.0, and (c) 7.4.

mer being the limiting case. The observed difference in the δ_P values in the ^{31}P NMR spectra can also be determined by a change in the composition of the inner coordination sphere of the complex (structures **B** and **C**) caused by the replacement of chloride ions by water molecules following a decrease in the overall concentration of the reactants and replacement of the water molecule by a hydroxyl group following an increase in the pH.

In the system with equimolar reactant ratio ($c_{K_2PdCl_4} = c_{NTMP} = 0.01$ mol/l), an increase in the concentration of chloride anions from 0.04 to 0.54 mol/l is accompanied by a decrease in the integral intensity of the ^{31}P NMR signals corresponding to coordinated phosphonic groups and an increase in the integral intensity of the ^{31}P NMR signals corresponding to phosphonic groups not bound to palladium(II) (table). These changes in the ^{31}P NMR spectra may attest to existence of an equilibrium between the complexes with structures **A** and **B** at a 50-fold excess of chloride anions. Evidently, in this case, one phosphonic group is displaced from the inner sphere of the complex with structure **B** by a chloride anion. Further addition of chloride anions to the system with maintenance of the same pH results in a shift in the equilibrium of complex formation towards the initial reactants ($[PdCl_4^{2-}]$, $[PdCl_3(H_2O)^-]$, $[H_4L^{2-}]$ $[H_3L^{3-}]$). Simultaneously, redistribution of the integral intensities of the signals of coordinated phosphonic groups (δ^{31}P at about 34–38 ppm) and the palladium(II)-uncoordinated phosphonic groups (7–9 ppm) was observed. This effect supports the assumption about the association. All ^{31}P NMR signals are broadened, apparently, due to participation of the phosphonic groups in the intra- and intermolecular exchange.

Note that in the ^{31}P–{^{1}H} NMR spectra of solutions with pH > 7, the signals of species with $\delta_P = 34.45$ ppm, $\Delta\nu = 116.2$ Hz and $\delta_P = 7.55$ ppm, $^2J_{PH} = 10.8$ Hz predominate (Fig. 1a). However the spectra exhibit also other signals whose δ and *I* values depend on the nature of the counter-ion (Fig. 4). In the case of excess of lithium cations, the spectrum shows two signals with δ_P of

Signal positions and integral intensities in the ^{31}P NMR spectra of the K_2PdCl_4–NTMP system*

c_{Cl^-}, mol/l	pH	Coordinated phosphonic groups		Uncoordinated phosphonic groups	
		δ^{31}P, ppm	*I*, %	δ^{31}P, ppm	*I*, %
0.04	4.21	38.10	33.7	7.79	35.8
		35.05	30.5		
0.14	4.23	37.30	48.7	7.50	36.4
		34.48	14.9		
0.54	4.27	36.02	53.5	7.15	11.8
				6.19	34.7

* $c_{K_2PdCl_4} = c_{NTMP} = 0.01$ mol/l.

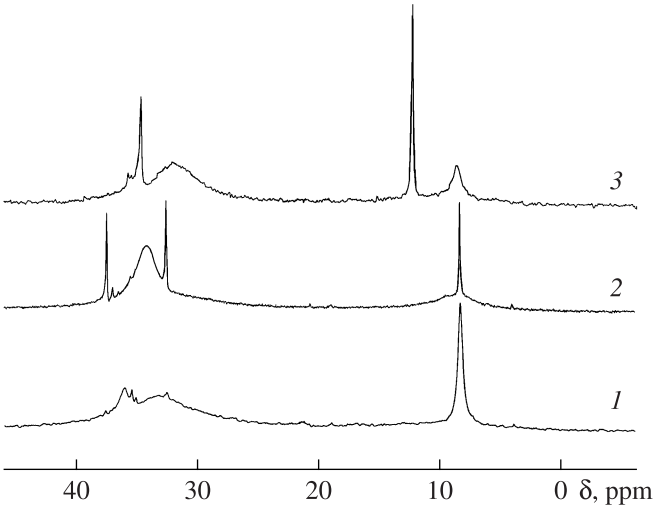


Fig. 4. ^{31}P NMR spectra of the K_2PdCl_4–NTMP–MOH system, $c_{K_2PdCl_4} = c_{NTMP} = 0.01$ mol/l, M = (*1*) $N(n\text{-Bu})_4^+$, (*2*) K^+, and (*3*) Li^+, pH 7.6.

34.80 and 12.19 ppm and the ratio $I = 1 : 2$. An excess of potassium cations gives rise to three signals ($\delta_P = 36.76$, 31.96, and 7.79 ppm with equal integral intensities), which change according to the same pattern as functions of pH. These signals appear in the spectra due to the increase in the concentration of alkali metal cations that form ion associates with molecules of the complex.

Binding of the potassium cations into ion associates with the negatively charged phosphonic oxygen atoms is facilitated by the less pronounced susceptibility for solvation compared to that of lithium ions. Presumably, as a result of this interaction, one phosphonic group of the ligand may become spatially located in the axial position of the coordination polyhedron. The ^{31}P NMR signal corresponding to this group occurs at 31.96 ppm. This δ value is intermediate between the values for in-plane coordinated (36.76 ppm) and free (7.79 ppm) phosphonic groups. Under these conditions, all three phosphonic groups are exhibited on the NMR time scale as separate narrow signals. One more reason supporting this explanation is the fact that in the ^{31}P NMR spectra recorded without proton decoupling, the signals considered are additionally split and are manifested as a doublet ($\delta_P = 36.76$ ppm., $^2J_{PH} = 15.42$ Hz), a doublet of doublets ($\delta_P = 31.92$ ppm, $^2J_{PH} = 4.33$ Hz, $^2J_{PH} = 18.80$ Hz), and a triplet ($\delta_P = 7.79$ ppm, $^2J_{PH} = 10.6$ Hz). Different values of the $^2J_{PH}$ constant of the CH_2 groups attests to the formation of two stable (on the NMR time scale) cyclic structures differing in the conformation and the spatial arrangement of the phosphonic groups with respect to the central atom. In the presence of lithium ions in the K_2PdCl_4–NTMP system, the ^{31}P NMR spectra showed a 1 : 2 ratio of the integral intensities of the Pd(II)-coordinated and uncoordinated phosphonic groups of NTMP. This ratio may be due to the formation of strong bonds by one coordinated phosphonic group in structure **B** with lithium ion and replacement of this group by a chloride anion (H_2O or OH^-) to give structure of type **A**.

The ^{31}P NMR spectra recorded in the presence of potassium cations could also be interpreted as a result of existence of a palladium complex with coordination number of 5. However, only few examples of formation of such complexes with polydentate ligands are known [24]. Note also that on attempted calculation, complexes with the inner sphere [Pd; 2Cl; N; 2O] or [Pd; Cl; N; 3O] are spontaneously converted during geometry optimization into conformational isomers with coordination number 4 more typical of palladium. This indicates that in the case of an isolated molecule and in the absence of interaction with a potassium cation, this type of coordination is not typical of the metal–ligand combination in question as this does not lead to the formation of structures corresponding to minima in the potential energy surface. On the other hand, it is now an extremely difficult task to take account of all of the possible conformers, ligand coordination modes, participation of water molecules, and effect of the counter-ions and to identify the most probable way of formation of di- and oligomers by quantum chemistry methods.

It is notable that when tetrabutylammonium was used as the base, no formation of stable associates was detected at all. Obviously, the bulky $N(n\text{-Bu})_4^+$ cation has a weakly pronounced tendency for association and the spectral signals are only broadened as a result of complex intra- and intermolecular interactions.

To obtain additional knowledge of the nature of processes taking place in the system, the temperature dependence of the ^{31}P NMR spectra of solutions containing equimolar amounts of the reactants at the pH of 3.60, 7.60, and 9.64 and $c_{Pd(II)} = 0.3$ or 0.01 mol/l was studied. As the temperature is raised, the ^{31}P NMR signals due to phosphonic groups with different degrees of involvement into exchange interactions coalesce (24 ppm). The effect of temperature is insignificant for the narrow signals corresponding to the complex in whose coordination sphere the exchange processes, as noted above, are slow on the NMR time scale (Fig. 5).

The ^{31}P NMR spectra of the system with K_2PdCl_4 : NTMP molar ratio of 1 : 2 show a similar signal evolution as a function of pH (Fig. 1b), which confirms the conclusion based on pH-potentiometric and spectrophotometric studies about the formation of equimolar complexes. The ratio of integral intensities of the ^{31}P NMR signals of phosphonic groups where two of the six groups present in the two reagent molecules are directly involved in the Pd(II) coordination sphere, while the other four groups remain free (or as noted

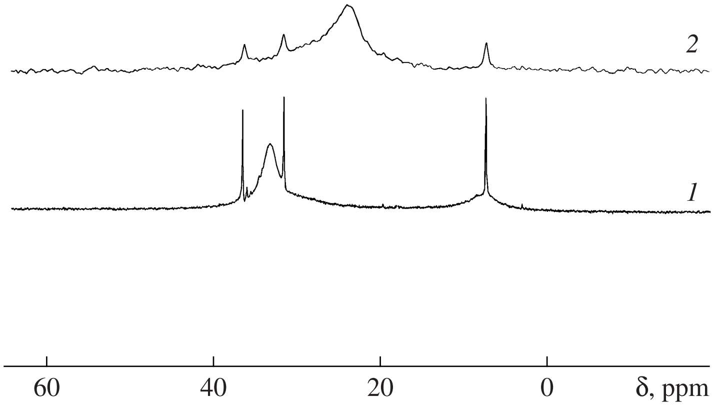


Fig. 5. Temperature dependence of the ^{31}P NMR spectra of the 1 : 1 K_2PdCl_4–NTMP system, $c_{K_2PdCl_4} = c_{NTMP} = 0.01$ mol/l; pH 7.6, T = (*1*) 20 and (*2*) 90°C.

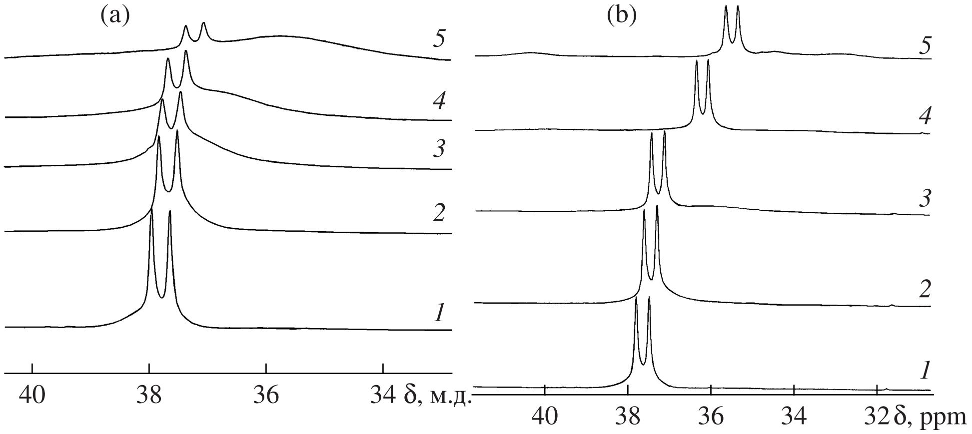


Fig. 6. ^1H NMR spectra of the K_2PdCl_4–NTMP system: (a) $c_{K_2PdCl_4} = c_{NTMP} = 0.1$ mol/l at pH (*1*) 1.80, (*2*) 2.63, (*3*) 3.02, (*4*) 3.24, (*5*) 3.66; (b) $c_{K_2PdCl_4} = 0.1$ mol/l, $c_{NTMP} = 0.2$ mol/l at pH (*1*) 2.28, (*2*) 2.94, (*3*) 3.44, (*1*) 5.72, (*6*) 6.72.

above are involved in outer-sphere interactions), is attained in the system with pH > 7.

^1H NMR spectra of the K_2PdCl_4–NTMP system. The ^1H NMR spectra of NTMP solutions at pH 1.06–7.60 exhibit a doublet for the protons of CH_2 groups with δ_H = 3.55–3.8 ppm and $^2J_{P–H}$ = 12.84 Hz. As pH increases, the ^1H NMR spectra of the K_2PdCl_4–NTMP system (1 : 1), in addition to the decrease in the integral intensity of the signal for the CH_2 groups of free NTMP and the change in the parameters in the ranges δ_H = 3.72–3.78 ppm and $J_{P–C–H}$ = 11.76–12.83 Hz, exhibit a new broadened signal with δ_H = 3.57–3.79 ppm and $\Delta\nu$ = 39–114 Hz (Fig. 6a). Note that at pH 3.66, the ratio of integral intensities of the signals for methylene protons (determined using signal resolution procedures) for the coordinated and free functional groups is ~2 : 1. The observed broadening of the signals for the coordinated $CH_2–P(O)_2O$ groups, as discussed above, is probably due to their exchange fast on the NMR time scale.

In the system with 1 : 2 reactant ratio, an increase in pH leads to a decrease in the intensity of the overall proton signal of free NTMP and an increase in the intensity of the proton signals for complexed NTMP (Fig. 6b). As follows from the integral intensity ratio of the ^1H signals of coordinated and free functional groups of NTMP, at pH 6.72 only two of the six phosphonic groups are involved in coordination to Pd(II), which confirms the formation of equimolar complexes in the given system.

Thus, the ^{31}P and ^1H NMR study of the K_2PdCl_4–NTMP system at 1 : 1 and 1 : 2 reactant ratios showed the formation of equimolar complexes with bidentate [N,O] and tridentate [N,O,O] ligand coordination. The coordination modes of NTMP to palladium(II) in the complexes depends on the concentrations of reactants (palladium(II) and the ligand) and chloride ions and on the pH. Complexes with bidentate NTMP coordination are formed in acidic solutions with high concentrations of chloride ions. In neutral solutions with a slight excess of chloride ions, complexes with tridentate coordination of NTMP to palladium were formed. For high concentrations of the reactants, the polynuclear complexes were shown to be formed with participation of coordinated phosphonic groups, the phosphonic groups not bound directly to palladium(II) but forming intermolecular hydrogen bonds, cations of the bases added to the system, and solvent molecules.

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