Coordination Compounds

The influence of the position of double bonds of unsaturated carboxylic acids on the type of the resulting coordination polymers of palladium(I)

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For the first time in the coordination chemistry of palladium, a new class of palladium(I) polymers with unsaturated monocarboxylic acids obtained by the interaction of palladium(II) acetate $Pd_3(\mu\text{-}MeCO_2)_6$ with monocarboxylic 3-pentenoic and 4-pentenoic acids with a double bond not conjugated with the carboxyl group, cinnamic and crotonic acids with a double bond conjugated with the carboxyl group was isolated, and the interaction with a dicarboxylic acid (itaconic) with a double bond conjugated with only one carboxyl group, similar to cinnamic and crotonic acids, was studied. Analysis of the composition of eight newly synthesized compounds, as well as their IR, Raman and EPR spectra showed that the obtained coordination polymers of Pd(I) $[Pd(RCOO)_6]_n$ with 3-pentenoic $\{[Pd(\pi\text{-}C_5H_7O_2)] \cdot H_2O\}_n$ and 4-pentenoic $[Pd(\pi\text{-}C_5H_7O_2) \cdot C_5H_8O_2)]_n$ acids are diamagnetic, and with cinnamic $[Pd(C_9H_7O_2)]_n$, crotonic $\{[Pd(C_4H_5O_2)]H_2O\}n$ and itaconic $\{[Pd(C_5H_4O_4)H_2O] \cdot 2H_2O\}n$ acids they are paramagnetic. The backbone of the obtained polymers is formed by bridging carboxylate groups and Pd–Pd bonds. The completion of the coordination polyhedron in the case of complexes with 3- or 4-pentenoic acid is carried out by coordinating their double bond with palladium, in polymer complexes with cinnamic and crotonic acids - by the formed agostic bond, in complexes with itaconic acid - by a coordinated water molecule. According to EPR spectroscopy, the polymer with itaconic acid contains paramagnetic centers characterized by a content of 10^{18} spin/g of unpaired electrons stable for a year, which allows it to be considered as a precursor for the creation of heterogeneous catalysts with increased catalytic activity.
Keywords: coordination polymers of Pd(I), unsaturated carboxylic acids, palladium carboxylates

INTRODUCTION

Among the large number of metals with carboxylic acids, unsaturated carboxylates occupy a special place. Unsaturated carboxylic acids are potentially polydentate ligands, since in addition to carboxyl groups, they have reactive unsaturated bonds in their structure. These features can be used in further functionalization of complexes for the construction of new promising materials. For example, carboxylate clusters of transition metals are considered as the basis of nanostructured

fragments of organo-inorganic films [1-4]. Not only mono- and dicarboxylates of transition metals with unsaturated substituents in the carboxylate ligand, but also those containing N-, P-, S-donor fragments are studied as microporous materials capable of occluding N_2, O_2, Ar and Xe [5-9].

Special attention in recent decades has been given to the study of the structure and properties of polynuclear complexes with agostic bonds. The study of the influence of intermediate complexes with agostic bonds that accelerate catalytic processes [10] in organic reactions opens up new possibilities for organometallic chemistry and organometallic catalysis.

Analysis of a large number of metal complexes with the M-H bond has allowed the classification of agostic bonds as a separate class, described as three-center two-electron bonds, depicted as M...H-C. Since the parameter values of the agostic bond M...H-C for Pd...H are 1.83-1.88 Å, Pd-C 2.352 Å, C···H 1.144 Å [11], the agostic bond was classified as a group of strong bonds [12-18], whereas weak hydrogen bonds M ··· H in Pd(II) and Ru(II) complexes are characterized by values of 2.81 and 2.70 Å, respectively [19, 20].

Another direction currently successfully developing in the study of catalytic processes is the investigation of transition metal systems with unpaired electrons. In early works, using the example of ethylene dimerization to butene, a significant acceleration of this process was shown by unpaired electrons appearing during irradiation in ion-exchange zeolites NaPd-X and CaPd-X doped with palladium aminate complexes [21]. The same influence of unpaired electrons in palladium-exchange zeolites was also recorded in CO hydrogenation [22-24], NO reduction [23], pyridine and acetonitrile reduction [25]. As a result of analyzing a large number of studies on the influence of unpaired electrons on the rate of catalytic processes, a new type of catalysis was formed - spin catalysis [26].

The experimental results presented below on the study of palladium compounds with unsaturated mono- and dicarboxylic acids show the possibility of forming Pd(I) coordination polymers with agostic bonds and unpaired electrons in their polymer matrix.

The first compounds with unsaturated monocarboxylic acids - trinuclear Pd(II) complexes $[Pd_3(\mu\text{-RCOO})_6]$ - were described in works [27, 28] and obtained by the interaction of Pd(II) acetate with crotonic, 1-methylcrotonic and cinnamic acids with double bonds conjugated with the carboxyl group in an aromatic solvent. According to elemental analysis, IR and Raman spectroscopy data, the coordination polymer in them is formed by bridging carboxylate groups. Double bonds do not participate in complex formation.

Our studies of the interaction of Pd(II) acetate with 4-pentenoic and sorbic acids with double bonds not conjugated with the carboxyl group in methanol at a reagent ratio of 1:1 showed that paramagnetic Pd(I) coordination polymers $\{[Pd(C_5H_7O_2)]H_2O\}_n$ are formed. The backbone of the obtained polymers is formed by bridging carboxylate groups, Pd-Pd bonds, and coordinated double bonds of acids [29].

EXPERIMENTAL PART

For the synthesis of unsaturated palladium carboxylates, we used palladium acetate $Pd_3(\mu\text{-}MeCO_2)_6$, obtained according to our developed method [28], $(C_6H_5CN)_2PdCl_2$ and acids: 3-pentenoic $CH_3\text{–}CH\text{=}CH\text{–}CH_2\text{–}COOH$ (**3-pent**), 4-pentenoic $CH_2\text{=}CH\text{–}CH_2\text{–}CH_2\text{–}COOH$ (**4-pent**), cinnamic $C_6H_5CH\text{=}CHCOOH$ (**cin**), crotonic $CH_3\text{–}CH\text{=}CH\text{–}COOH$ (**crot**), itaconic $HOOC\text{–}CH_2\text{–}C(\text{=}CH_2)\text{–}COOH$ (**itak**) from Sigma-Aldrich. Methyl alcohol, acetone, benzene, toluene, hexane, benzonitrile, and petroleum ether from Khimmed were used as solvents.

Elemental analysis was performed on a Carlo Erba Instruments Chnsoea 1108 analyzer.

IR spectra of crystalline samples were recorded in the range of 4000-550 cm^{-1} using the ATR method on a NEXUS FTIR spectrometer from Nicolet (single-beam, scanning, CsI beam splitter, TGS-CsI detector, photometric accuracy 0.1%, resolution 2 cm^{-1}) using a MIRacle accessory from PIKETechnologies with a diamond crystal. Samples were applied directly to the diamond crystal without additional sample preparation.

Raman spectra were recorded on an in Via Reflex Renishaw instrument: 100× objective, irradiated area ~10 μm in diameter, excitation source power <100 μW. A He-Ne laser with a wavelength of 633 nm was used as the source. For signal detection, a Peltier-cooled CCD matrix was used, with spectral resolution of 2 cm^{-1}.

EPR spectra of the compounds were recorded using a Bruker Elexsys E680X EPR spectrometer in the X-band (operating frequency ~9.8 GHz) at room temperature. The studied substances were placed in quartz ampoules and stored in ampoules throughout the experiment. Heating to 40°C was carried out directly in the ampoules. The spectra of the studied compounds were corrected taking into account the spectrum of an empty resonator. The concentration of unpaired electrons was determined by double integration of EPR spectra and subsequent analysis of the results using the Spin-Count function of the EPR spectrometer, calibrated with a Bruker Alanine Spin Concentration Sample standard with an unpaired electron concentration of 1.75×10^{17} (± 10%).

Differential thermal analysis was performed on a SDT Q600 synchronous thermal analyzer (TA Instruments) at a heating rate of 5 degrees/min in the temperature range from 30 to 400 or 800°C in argon.

Synthesis of {[Pd(π-C$_5$H$_7$O$_2$)]. H$_2$O}$_n$ (1). To a solution of 224 mg (1 mmol) of Pd(CH$_3$COO)$_2$ in 20 ml of methanol, 0.1 ml (1 mmol) of **3-pent** was added. After stirring at 20-25°C for 2 h, the reaction mixture was kept at +6°C for 20 h until a light brown precipitate formed, which was filtered through a Schott filter No.16, washed with benzene (3 × 10 ml) and dried under vacuum at 0.7 mm Hg to constant weight. The yield was 82%.

Found, %:   C 27.12;   H 3.60.

For C$_5$H$_9$O$_3$Pd calculated, %:   C 26.86;   H 3.43.

IR spectrum (ν, cm^{-1}): 1565, 1555 ν_{as}(COO$^-$), 1394 ν_s(COO$^-$), 3400-3200 ν(HOH).

Raman spectrum (ν, cm^{-1}): 1518 ν(C=C), 366 ν(Pd-Pd).

Synthesis of [*transPdCl* PdCl$_2$(π-C$_5$H$_8$O$_2$)(H$_2$O)] (2). To a solution of 383 mg (1 mmol) of (C$_6$H$_5$CN)$_2$PdCl$_2$ in 20 ml of benzene, 0.3 ml (3 mmol) of **3-pent** was added with stirring. The synthesis was carried out for 30 h at 20-25°C until formation of yellow precipitate. Further according to the synthesis procedure of **1** . Yield 65%.

Found, %: C 23.34; H 2.80.

For C$_5$H$_{10}$O$_3$Cl$_2$Pd calculated, %: C 20.32; H 3.41.

IR spectrum (ν, cm^{-1}): 1678 ν(C=O), 1519 ν(C=C), 338 ν(Pd-Cl), 3400-3200 ν(HOH).

Synthesis of { [Pd(π-C$_5$H$_7$O$_2$)] · C$_5$H$_8$O$_2$}$_n$ (3). To a solution of 224 mg (1 mmol) of Pd(CH$_3$COO)$_2$ in a mixture of 20 ml toluene + 20 ml hexane, 0.2 ml (2 mmol) of **4-pent** was added with stirring. The synthesis was carried out for 4 h at 20-25°C until formation of light brown precipitate. Further according to the synthesis procedure of **1** . Yield 82%.

Found, %:   C 39.22; H 4.78.

For C$_{10}$H$_{15}$O$_4$Pd calculated, %: C 39.43; H 4.63.

IR spectrum (ν, cm^{-1}): 1545 ν_{as}(COO$^-$). 1417 ν_s(COO$^-$). 1756 ν(C=O).

Raman spectrum (ν, cm^{-1}): 1518 ν(C=C), 335 ν(Pd-Pd).

Synthesis of [PdCl$_2$(π-C$_5$H$_8$O$_2$)][[513]]2$_2$ (4). To a solution of 383 mg (1 mmol) of (C$_6$H$_5$CN)$_2$PdCl$_2$ in 20 ml of benzene, 0.5 ml (5 mmol) of **4-pent** was added with stirring. The synthesis

was carried out for 3 h until formation of dark orange precipitate, which was filtered, washed with benzene and petroleum ether. Further according to the synthesis procedure of **1** . The yield was 83%. Found, %: C 21.47; H 2.69.

For $C_{10}H_{16}O_4Cl_2Pd_2$, calculated, %: C 21.64; H 2.90.

IR spectrum (v, cm^{-1}): 1697 v(C=O); 1520 v(C=C); 350, 319, 302 v(Pd-Cl).

Synthesis of [Pd($C_9H_7O_2$)] $_n$(5). To a solution of 224 mg (1 mmol) $Pd_3(CH_3CO_2)_6$ in 20 mL of methanol, 148 mg (1 mmol) of **cinnamaldehyde** was added. The reaction mixture was stirred at 20-25°C for 24 h until an orange precipitate formed. Further according to the synthesis procedure of **1** . Yield 57%.

Found, %:   C 42.06;   H 3.59.

For $C_9H_7O_2$Pd calculated, %: C 42.69;   H 2.77.

IR spectrum (v, cm^{-1}): 1566, 1538 v_{as}(COO$^-$); 1386 v_s(COO$^-$); 1634 v(C=C).

Raman spectrum (v, cm^{-1}): 1636 v(C=C), 360 v(Pd-Pd).

Synthesis of {[Pd($C_4H_5O_2$)] $\cdot$ H_2O}$_n$(6). To a solution of 224 mg (1 mmol) Pd(CH$_3$CO$_2$)$_2$ in 20 mL of methanol, 86 mg (1 mmol) of **crotonic acid** was added. Further according to the synthesis procedure of **1.** Yield 45%.

Found, %:   C 22.64;   H 2.42.

For $C_4H_7O_3$Pd calculated, %: C 22.97;   H 3.35.

IR spectrum (v, cm^{-1}): 1575, 1533 v_{as}(COO$^-$); 1385 v_s(COO$^-$); 1640 v(C=C); 3400-3100 v(HOH).

Raman spectrum (v, cm^{-1}): 1646 v(C=C), 323 v(Pd-Pd).

Synthesis of {[Pd($C_5H_4O_4$)H_2O] $\cdot$ $2H_2O$}$_n$(7). To a solution of 224 mg (1 mmol) Pd(CH$_3$COO)$_2$ in 20 mL of methanol with stirring, 148 mg (1 mmol) of **itaconic acid** was added. The complex synthesis was carried out at 20-25°C for 24 h until an orange precipitate formed. Further according to the synthesis procedure of **1** . Yield 57%.

Found, %:   C 20.32; H 3.27.

For $C_5H_{10}O_7$Pd calculated, %: C 20.82;   H 3.47.

IR spectrum (ν, cm^{-1}): 1528 ν_{as}(COO$^-$); 1390 ν_s(COO$^-$); 3400-3000 ν(HOH).

Synthesis of [Pd$_3$(C$_5$H$_5$O$_4$)$_6$] (8). A solution of 224 mg (1 mmol) of Pd(CH$_3$COO)$_2$ in 20 ml of benzene and 260 mg (2 mmol) of itaconic acid was placed in a round-bottom flask. The complex synthesis was carried out at 45°C for 6 h until an orange precipitate formed. Further according to the synthesis procedure of **So**. The complex was synthesized at 45°C for 6 hours until an orange precipitate formed. Then, according to the synthesis method, **1.** Yield 48%.

Found, %:   C 33.48;   H 3.80.

For C$_{30}$H$_{30}$O$_{24}$Pd$_3$ calculated, %: C 33.15;   H 2.22.

IR spectrum (ν, cm^{-1}): 1696 ν(C=O); 1594 ν_{as}(COO$^-$); 1412, 1395 ν_s(COO$^-$).

RESULTS AND DISCUSSION

To determine the influence of double bonds position in unsaturated monocarboxylic acids and synthesis conditions on the nature of formed compounds, eight new coordination polymers of Pd(I) and Pd(II) complexes were synthesized and studied: with **3-pentenoic** and **4-pentenoic** acids with one double bond not conjugated with the carboxyl group; with **cinnamic** and **crotonic** acids with a double bond conjugated with the carboxyl group, and **itaconic** acid with a double bond conjugated with only one carboxyl group, with a fragment similar to that in cinnamic and crotonic acids.

The interaction of **3-pentenoic** acid (CH$_3$-CH=CH- CH$_2$-COOH) with Pd(II) acetate in methanol leads to the formation of Pd(I) coordination polymer {[Pd(π-C$_5$H$_7$O$_2$)][[848]]]·H · H$_2$O}$_n$ (**1**) (Fig. 1), which is confirmed by the results of microanalysis, IR and Raman spectroscopy, as well as TGA data. The IR spectrum of **1** contains bands ν_{as}(COO$^-$) at 1565, 1555 cm^{-1} and ν_s(COO$^-$) at 1394 cm^{-1}, indicating the formation of bridging carboxyl groups of **3-pentenoic** acid in **1** .

In the IR spectrum of **1** , a band at 366 cm^{-1} is observed, which corresponds to the stretching vibrations of the Pd(I)-Pd(I) bond, as well as a band at 1518 cm^{-1}, corresponding to the palladium(I)-coordinated double bond.

The presence of a solvate water molecule in **1** is indicated in the IR spectrum by a broad band at 3400-3700 cm^{-1}. According to TGA data, the endothermic process at 100°C is accompanied by the loss of a solvate water molecule with a mass loss of 6.5%. The complete loss of the water molecule corresponds to a mass loss of 8.4%, however, this process overlaps with the exothermic decomposition process of **1** , which begins at 115°C.

To confirm the correct assignment in the IR spectrum of **1** of the coordinated C=C double bond band at 1518 cm $^{-1}$ lying in the frequency region of bridging carboxylate groups stretching vibrations in the range of 1500 - 1565 cm $^{-1}$, a known method of substituting the benzonitrile ligand in $(C_6H_5CN)_2PdCl_2$ with an unsaturated ligand was applied. This method will be used further in the article, as in the presence of chloride ion, the error in selecting the frequency of coordinated double bond vibrations in the presence of bridging carboxylate groups frequencies is eliminated. In the reaction of **3-pent** with $(C_6H_5CN)_2PdCl_2$, a mononuclear complex $[PdCl_2(\pi\text{-}C_5H_8O_2)(H_2O)]$ (**2**) is formed (Fig. 2). In the IR spectrum of **2**, a band of the coordinated double bond ν(C=C) is observed at 1518 cm $^{-1}$, confirming the correct assignment of this band to the coordinated double bond in the coordination polymer **1**. The ν(OH) band at 3188 cm $^{-1}$ indicates the presence of a coordinated water molecule in **2**. The broad band at 3100-2600 cm $^{-1}$ in **1** characterizes intermolecular hydrogen bonds of free carboxyl groups -COOH between two adjacent complexes **1**.

Investigation of coordination polymer **1** revealed its identity (in composition and structure) to Pd(I) coordination polymer with **4-pent** [29], which indicates no influence of the double bond position in the hydrocarbon radical on the coordination polymer composition.

Comparative study of EPR spectra **1** and the aforementioned polymer with **4-pent** shows that both are paramagnetic. The broadening of EPR spectra of both polymers is a result of interaction between paramagnetic Pd(I) ions, indicating incomplete formation of Pd-Pd bonds in these polymers. Both coordination polymers contain practically the same amount of unpaired electrons: 1.06×10^{17} spin/g in **1** and 3.03×10^{17} spin/g in polymer with **4-pent**. The above data indicate that shifting the double bond in **3-pent** by one carbon-containing group towards the carboxyl group does not affect the rate of Pd-Pd bond formation in them.

In the interaction of **4-pent** (CH_2=CH-CH$_2$- CH$_2$-COOH) with Pd(II) acetate in a mixture of toluene and hexane at a reagent ratio of 2:1, a Pd(I) coordination polymer $\{[Pd(\pi\text{-}C_5H_7O_2)] \cdot C_5H_8O_2\}_n$ (**3**) is formed. The IR spectrum of **3** shows vibration bands of bridging carboxyl groups at 1545 cm $^{-1}$ ν_{as}(COO$^-$) and 1415 cm $^{-1}$ ν_s(COO$^-$). The Raman spectrum of **3** contains Pd-Pd bond vibration bands at 336 cm $^{-1}$ and a vibration band of the coordinated double bond in **4-pent** at 1518 cm $^{-1}$, forming coordination polymer **3**. The solvate molecule of **4-pent** is characterized by the band ν(C=O) at 1765 cm $^{-1}$, close in value to ν(C=O) at 1789 cm $^{-1}$ for gaseous **4-pent**.

To clarify the correct assignment of the band ν_{coord}(C=C) at 1518 cm $^{-1}$ in **3**, a chloride complex $[PdCl_2(\pi\text{-}C_5H_8O_2)]_2$ (**4**) was synthesized. The position of the band ν_{coord}(C=C) at 1518 cm $^{-1}$ in **3** coincides with its position at 1520 cm $^{-1}$ in the IR spectrum of the synthesized binuclear complex [PdCl

$_2(\pi\text{-}C_5H_8O_2)]_2$ (**4**). The band of uncoordinated carboxyl group $\nu(C=O)$ at 1697 cm^{-1} is somewhat lower compared to its position in dimer **4** (1704 cm^{-1}), which is a result of the formation of strong intermolecular hydrogen bonds between two carboxyl groups of adjacent molecules **4** . The dimeric structure of **4** is confirmed by the presence in its IR spectrum of bands of two types of Pd-Cl bonds: $\nu(\text{Pd-Cl})_{terminal}$ at 350 cm^{-1} and $\nu(\text{Cl-Pd-Cl})_{bridge}$ at 319 and 302 cm^{-1} (Fig. 3).

The solvate nature of molecule **4-pent** in **3** is also confirmed by TGA data. The mass loss process of **3** begins at a temperature of 84°C, identical to the boiling point of free **4-pent** . Temperature increase to 117-135°C is accompanied by an exothermic decomposition process of **3** with a total mass loss of 60.4%. Analysis of the residue after decomposition of **3** showed a carbon content of 10.16%, which corresponds to the theoretical carbon content in palladium carbide PdC of 10.14%. However, this result requires further investigation, since previously thermal decomposition of Pd(II) polymers resulted in the formation of Pd oxide or metallic Pd as residue.

Comparative EPR study **3** with solvate molecule **4-pent** and its analogue $\{[\text{Pd}(C_5H_7O_2)] \cdot H_2O\}$ with water solvate molecule [29] showed that both Pd(I) polymers contain paramagnetic centers characterized by different unpaired electron content. The content of unpaired electrons in **3** (2.14×10^{15} spin/g) is three orders of magnitude lower than in its analogue with water solvate molecule (3.03×10^{18} spin/g), which indicates acceleration of Pd-Pd bond formation in polymer **3** in the presence of solvate molecule **4-pent** . It should be noted that the transformation of **3** from paramagnetic to diamagnetic occurs within 4 months during storage at room temperature, i.e., the completion of Pd-Pd bonds is possible in the solid phase.

As a result of the interaction of Pd(II) acetate with unsaturated monocarboxylic acids **cin** ($C_6H_5CH=CHCOOH$) and **crot** ($CH_3-CH=CH-COOH$), containing double bonds conjugated with the carboxyl group, at a reagent ratio of 1:1 in methanol, diamagnetic coordination polymers of Pd(I) with **cin**][$\text{Pd}(C_9H_7O_2)$] (**5**) and **crot** $\{[\text{Pd}(C_4H_7O_2)]H_2O\}$ (**6**). Polymer chains are formed by bridging carboxylate groups, which are characterized in IR spectra by bands $\nu_s(COO)$ at 1386 cm^{-1} and $\nu_{as}(COO)$ lying in the frequency range of 1575-1500 cm^{-1}. Unlike the IR spectra of Pd(I) coordination polymers **1** and **3** with monocarboxylic acids **3-pent** and **4-pent** , the $\nu_{as}(COO)$ bands in the spectra of **5** and **6** split into three bands: 1571, 1555, 1511 cm^{-1} in **5** and 1575, 1537, 1505 cm^{-1} in **6** . The splitting can be explained by the influence of strong *trans* -positioned agostic Pd…H–C bonds on the carboxyl groups, formed in **5** by the terminal CH-group of the benzene ring of **cin** , and in **6** by the proton of CH$_3$-group of **crot** . The formation in **5** of the agostic Pd…H–C bond by the CH-group of

the benzene ring of **cin** causes the disappearance in the spectrum of **5** of the ν(Ph) band at 1599 cm $^{-1}$, which appears in the IR spectrum of free **cin** . Changes in band positions in the IR spectra of **crot** are also observed during the formation of coordination polymer **6** with an agostic bond. Thus, the singlet band δ(CH **crot** at 1428 cm $_3$) present in the IR spectrum of $^{-1}$ in the spectrum of **6** splits into three bands: at 1443, 1435, and 1421 cm $^{-1}$, which is caused by the participation of one of the hydrogen atoms of the methyl group of **crot** in the formation of the agostic Pd…H–C bond in the coordination polymer.

The formation of agostic bonds in complexes **5** and **6** leads to changes in the spectra in the frequency range of 3100-2800 cm $^{-1}$, where characteristic ν(CH) bands are recorded. For example, in the IR spectrum of complex **5** the C-H stretching vibration band of the benzene ring is shifted to the low-frequency region to 3050 cm $^{-1}$ compared to its value in the spectrum of **cin** at 3067 cm $^{-1}$. Similarly, in the spectrum of **6** the bands ν_{as}(CH$_3$) (2955 cm $^{-1}$) and ν_s(CH$_3$) (2813 cm $^{-1}$) are shifted to the low-frequency region relative to the corresponding bands (2976 and 2895 cm $^{-1}$) in the spectrum of **crot** .

According to IR spectroscopy data, the C=C double bonds of **cin** and **crot** do not participate in the formation of **5** and **6** . This is evidenced by both the C=C double bond vibration bands at 1634 (**5**) and 1647 cm $^{-1}$(**6**) in IR spectra, and the ν(C=C) bands at 1634 (**5**) and 1647 cm $^{-1}$(**6**) in Raman spectra, identical to the double bond vibration bands ν(C=C) at 1627 cm $^{-1}$(**cin**) and 1653, 1636 cm^{-1}(**crot**) in IR spectra. Similar positions of double bond vibration bands were found in the spectra of trinuclear Pd(II) complexes with **cin** (1632 cm $^{-1}$) and **crot** (1646 cm $^{-1}$) [28].

The frameworks of coordination polyhedra **5** and **6** are also formed by Pd-Pd bonds, manifesting in Raman spectra as ν(Pd-Pd) bands at 323 (**5**) and 360 cm $^{-1}$(**6**) (Fig. 4).

The presence of a solvate water molecule in **6** is confirmed in the IR spectrum by a broad ν(OH) band at 3400-3200 cm $^{-1}$, as well as by TGA data. At 70°C, **6** shows a mass loss of ~7%, corresponding to the loss of one water molecule. Further heating of **6** to 125°C leads to decomposition of **6** , accompanied by an exothermic effect at 120-140°C on the thermogram. Comparative analysis of thermal stability (according to TGA data) of coordination polymers **1** , **3** , **5** and **6** indicates higher thermal stability of **5** and **6** (with agostic bond) compared to **1** and **4** (with coordinated double bond), whose thermal decomposition begins already at 84-115°C respectively.

To compare the nature of coordination polymers **5** and **6** , formed by monocarboxylic acids with a double bond conjugated to the carboxyl group, the interaction of palladium acetate with **itaconic acid (** HOOC-CH$_2$-C(=CH$_2$)-COOH) - a dicarboxylic acid in which the double bond is conjugated with only one carboxyl group similar to the fragment in **cinnamic** and **crotonic** acids was studied. However, the presence of a second carboxyl group in **itaconic acid** may affect the composition and properties of the formed **itaconic acid** Pd(I) coordination polymer.

When **itaconic acid** interacts with Pd(II) acetate in methanol at a reagent ratio of 1:1, a Pd(I) coordination polymer $\{[Pd(C_5H_4O_4)H_2O] \cdot 2H_2O\}_n$(**7**) is formed. In the IR spectrum of **7** , only carboxylate group bands are observed: ν_{as}(COO$^-$) at 1525 cm^{-1} and ν_s(COO$^-$) at 1394 cm^{-1}, which indicates the participation of both carboxylate groups in the formation of **7** , similar to Pd(I) coordination polymers with maleic, fumaric, and citraconic acids [30]. In the coordination polymer, the double bond of **itaconic acid** does not participate in the formation of **7** , as evidenced by the identical double bond vibration bands and the double bond vibration frequency ν(C=C) at 1628 cm^{-1} in the spectra of **7** and **itaconic acid** . The presence of water molecules in **7** is characterized by a broad ν(OH) band in the region of 3400-3000 cm^{-1}(Fig. 5).

The loss of two solvate water molecules in **7** should be 13%, however, the thermogram shows only a 9% mass loss, as this endothermic effect is overlapped by the exothermic decomposition process of **7** at 130°C during further heating. The mass loss of **7** upon heating to 500°C is 48.3%, which corresponds to the formation of a residue containing only Pd$_{metal}$.

Interaction **itac** with Pd(II) acetate in benzene is accompanied by the formation of trinuclear Pd(II) complex [Pd$_3$(C$_5$H$_4$O$_4$)$_6$] (**8**), in which only one carboxyl group is coordinated, as confirmed by the presence of vibration bands ν_{as}(COO) at 1594 cm^{-1} and ν_s(COO) at 1412 cm^{-1} in its IR spectrum. The presence of an uncoordinated carboxyl group is confirmed in the IR spectrum of **8** by ν(C=O) vibrations at 1696 cm^{-1} and ν_{as}(COO) at 1395 cm^{-1}(Fig. 6).

The Pd(I) coordination polymer with **itac** is characterized by the presence of diamagnetic centers containing 5.88×10^{18} spin/g unpaired electrons, the amount of which remains stable for more than a year of polymer storage at room temperature, which is of undoubted interest for their use as precursors of heterogeneous catalysts for organic reactions.

Thus, the work shows that the interaction of Pd(II) acetate with unsaturated monocarboxylic acids **3-pent** , **4-pent** and dicarboxylic acid **itac** in methanol results in the formation of Pd(I)

coordination polymers, formed by bridging carboxyl groups and Pd-Pd bonds. The completion of coordination polymers **1** and **3** with monocarboxylic acids with double bonds not conjugated to the carboxyl group is carried out by double bonds coordinated by palladium. In the case of monocarboxylic acids with double bonds conjugated to the carboxyl group, coordination polymers **5** and **6** are supplemented by agostic bonds. In the case of dicarboxylic acid with a double bond conjugated to only one carboxyl group, coordination polymer **7** is formed by both carboxylate groups and is completed by a water molecule coordinated by palladium.
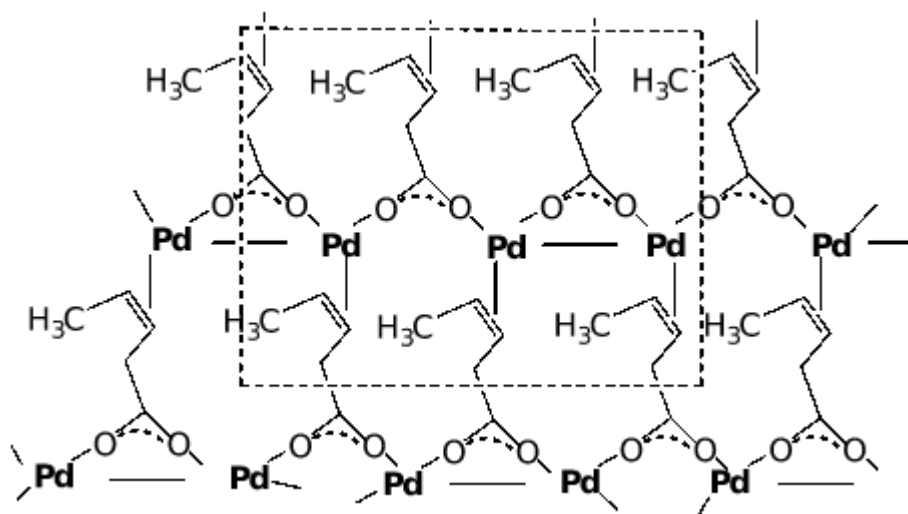
FUNDING

CONFLICT OF INTEREST

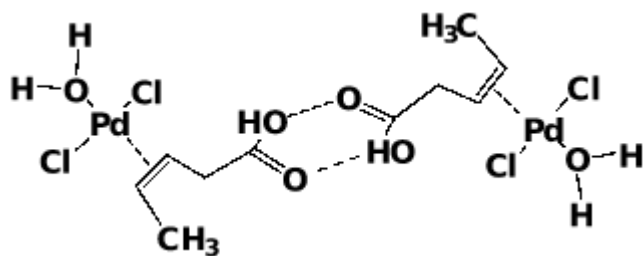The authors declare that they have no conflict of interest.

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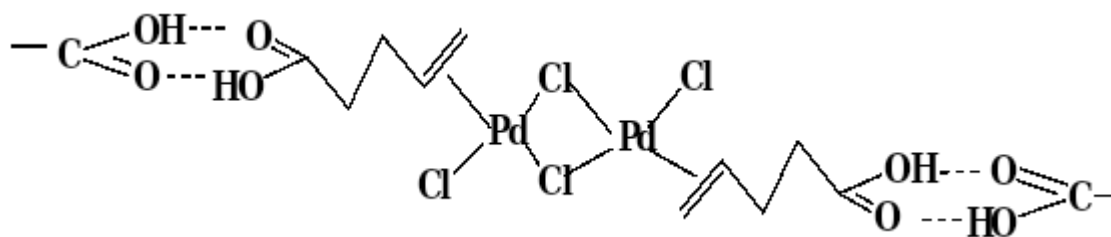14. *Sajjad M., Schwerdtfeger P., Harrison J. et al.* // Polyhedron. 2018. V. 151. P. 68.

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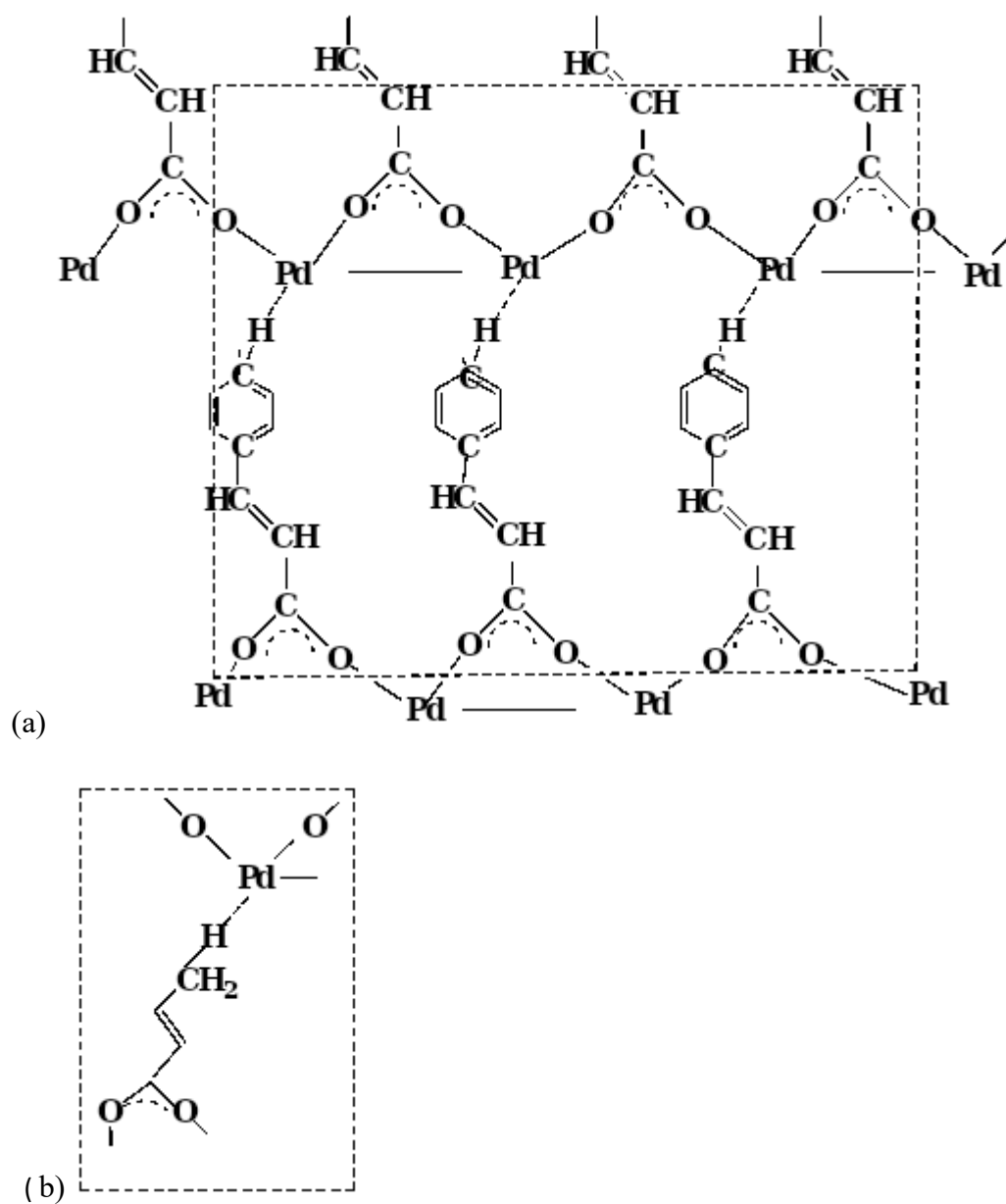
Fig. 1. View of the infinitely developing in two directions building block of Pd(I) coordination polymer with **3-pent** (**1**).
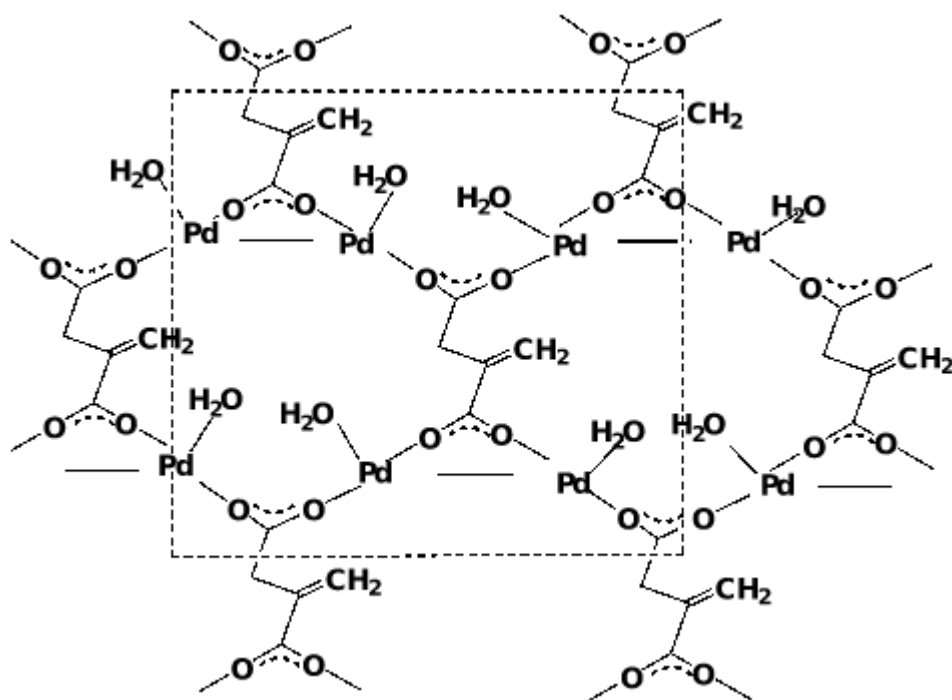

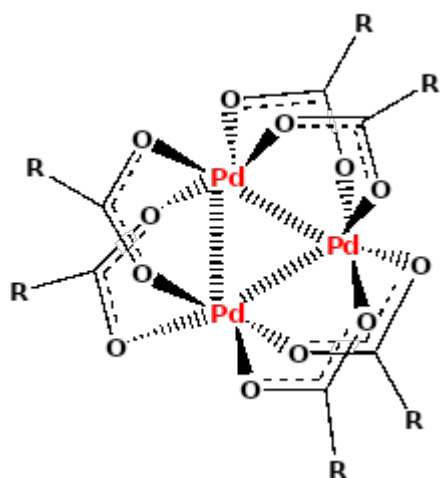**Fig. 2.** Structure of Pd(II) complex with **3-pent** (**2**).

Fig. 3. Structure of Pd(II) complex with **4-pent** (**4**).

Fig. 4. View of the infinitely developing in two directions building block of Pd(I) coordination polymers: a – with **cin** (**5**), b – fragment of the agostic bond structure in Pd(I) coordination polymer with **crot** (**6**) with identical structure to **5** .

Fig. 5. View of the infinitely developing in two directions block of Pd(I) coordination polymer with **itac** (**7**).

Fig. 6. Structure of trinuclear Pd(II) complex with **itac** (**8**).