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Palladium(I) Coordination Polymers with Unsaturated Dicarboxylic Acids with Stable Paramagnetic Centers

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Abstract—Palladium(I) coordination polymers with unsaturated dicarboxylic acids, $\{[cis\text{-}Pd(C_4H_2O_4)(H_2O)]\cdot(H_2O)\}_n$ (**I**) (maleic acid), $\{[cis\text{-}Pd(C_5H_4O_4)(H_2O)]\cdot 2H_2O\}_n$ (**II**) (citraconic acid), and $\{[trans\text{-}Pd(C_4H_2O_4)(H_2O)]\cdot(H_2O)\}_n$ (**III**) (fumaric acid) with stable paramagnetic centers in the polymer matrix were synthesized for the first time. According to IR and ESR spectroscopy data (determining the number of paramagnetic centers) and results of thermogravimetric analysis, the building blocks of **I**–**III** are, at least, tetranuclear Pd(I) clusters, in which palladium atoms are linked by bridging carboxylate groups. Each carboxylate group is coordinated via only one O atom, while the second O atom is linked to the nearest palladium atom of the neighboring cluster, thus giving a multidimensional coordination polymer. The coordination sphere of each Pd(I) atom in the cluster is completed by a water molecule and Pd–Pd bond. Heating of **I**–**III** results in the loss of solvation water molecules as the first stage. Above 100°C, the onset of removal of the coordinated water molecules is accompanied by complete decomposition of the complexes. On treatment of **I** with CH_3CN in methanol, redox reaction takes place, in which complex **I** disproportionates to give Pd(II) complex and Pd(0) to give $[Pd(HOOC{-}CH{-}CH(CH_3O)(CH_3CN)_2]$ (**IV**) (CIF file CCDC no. 2039147).

Keywords: Pd(I) dicarboxylate polymers, stable unpaired electrons, X-ray diffraction

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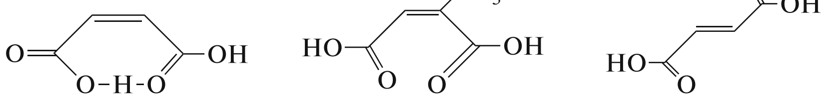
INTRODUCTION

The term “coordination polymers” was introduced in coordination chemistry by J.C. Bailar in 1964 [1]. The last decade has seen quite a number of publications dealing with coordination polymers, which have now become the basis of a new trend of materials science: design of metal-organic frameworks, which attract attention of researchers by the wide scope of practical applications. The active studies of the chemistry of coordination polymers of the last decade have been stimulated by their structural diversity [2] and unique functional characteristics [3] such as magnetism [4–9], conductivity [10, 11], various fields of optoelectronics [12], and catalytic and biometric systems [13]. These materials combine various metal centers and organic linkers. The linkers widely used now are aliphatic and aromatic carboxylates. Unsaturated dicarboxylates are little studied in this respect. Meanwhile, unsaturated macromolecular carboxylates contain, apart from the metal–carboxylate bond, also multiple bonds potentially capable of opening and thus enabling the formation of new structures with interesting physical properties [14, 15]. The main results concerning the use of unsaturated acids as linkers are described in monographs and reviews in relation to complexes of alkali, alkaline earth, and some transition metals [16–20].

Maleic, citraconic, and fumaric acids with a conjugated double bond, being polydentate ligands, can be used as organic linkers that are coordinated to metal atoms giving frameworks of various topologies, because of different positions of functional groups in their molecules. The structures of these dicarboxylic acids are shown in Scheme 1.



Maleic acid   Citraconic acid   Fumaric acids

Scheme 1.

2D and 3D polymeric Fe, Co, Ni, Cu, Mn, and Ag maleates and fumarates showed a wide diversity of frameworks [2, 7, 13, 21–26]. Studies of Cu(II), Mo(II), Ru(II, III), and Rh(II) dicarboxylates indicated the possibility of designing porous materials in which pore size and occlusion ability would be determined by the natures of both the metal and the dicarboxylic acid [22, 23].

As regards palladium carboxylates, in our previous studies, we showed that the reaction of Pd(II) acetate with unsaturated monocarboxylic acids in acetone gives trinuclear Pd(II) clusters $[PdL_2]_3$ with bridging carboxylate groups [27]. The reactions with unsaturated dicarboxylic (maleic and citraconic) acids in acetone in the presence of an excess of the acid yield Pd(II) polymeric complexes $[PdL_2H_2O]_n$, in which one acid molecule is bound to Pd(II) via both bridging caboxylate groups, while the other one is bound via only one carboxylate group. The second deprotonated group of this acid is hydrogen-bonded to the coordinated H_2O molecule of the nearest Pd atom [28].

To our knowledge, no data on Pd(I) complexes with dicarboxylic acids can be found in the literature. The first Pd(I) coordination polymers were prepared in our study by reactions of Pd(II) acetate with monocarboxylic (sorbic and 4-pentenoic) acids in methanol. An ESR study detected stable paramagnetic centers in the polymer matrix of these products [29]. It was shown [30, 31] that unpaired electrons can appear only upon irradiation of exchange zeolites (NaX, CaX) doped with K_2PdCl_4 single crystals at a temperature not exceeding 77 K. In [32], NaPdX and CaPdX zeolites were found to exhibit high catalytic activity for ethylene dimerization to *n*-butene. In the first step of dimerization, paramagnetic species $Pd^+C_2H_4$ and $Pd^+(C_2H_4)_2$ are formed in situ, and after completion of the reaction, they are converted to paramagnetic species $Pd^+C_4H_8$ and then palladium is reduced to Pd(0).

The present study continues our research dealing with Pd(I) polymeric complexes with unsaturated carboxylates contaning stable Pd^+ paramagnetic centers in the matrix. We developed methods for the synthesis of Pd(I) polymeric complexes with dicarboxylic acids (maleic, citraconic, and fumaric acids) and investigated the formation conditions and stability of paramagnetic centers and transformations in the Pd(I) polymer matrix.

EXPERIMENTAL

Palladium complexes with *cis*-maleic ($C_4H_4O_4$), *cis*-citraconic ($C_5H_6O_4$), and *trans*-fumaric ($C_4H_4O_4$) acids were prepared using palladium acetate $Pd_3(\mu\text{-}MeCO_2)_6$, which was obtained by the procedure we developed previously [27]. Commercial maleic, citraconic, and fumaric acids (Sigma-Aldrich) and methanol, acetone, and acetonitrile (Khimmed) were used as received.

Synthesis of $\{[cis\text{-}Pd(C_4H_2O_4)(H_2O)]\cdot(H_2O)\}_n$ (I). A solution of $Pd_3(CH_3CO_2)_6$ (0.224 g, 1 mmol) in CH_3OH and maleic acid (0.116 g, 1 mmol) were placed into a round-bottom flask. The solution was stirred at room temperature for ~2.5 h until a light brown precipitate formed. The precipitate was collected on a glass filter no. 16, washed with methanol (3 × 10 mL), and dried in vacuum. The product yield was 56%.

For $C_4H_7O_6Pd$		
Anal. calcd., %	C, 18.65	H, 2.74
Found, %	C, 18.09	H, 2.86

Synthesis of $\{[cis\text{-}Pd(C_5H_4O_4)(H_2O)]\cdot 2H_2O\}_n$ (II) was carried out by a procedure similar to that used for **I** starting from equimolar amounts of $Pd_3(CH_3CO_2)_6$ (0.224 g, 1 mmol) and citraconic acid (0.130 mL, 1 mmol) in CH_3OH. The synthesis was conducted for not more than ~1.5 h until a light brown precipitate formed. At longer reaction times, palladium in the reaction solution started to be reduced to Pd_{met}. The product yield was 68%.

For $C_5H_{10}O_7Pd$		
Anal. calcd., %	C, 20.81	H, 3.49
Found, %	C, 20.56	H, 3.39

Synthesis of $\{[trans\text{-}Pd(C_4H_2O_4)(H_2O)]\cdot(H_2O)\}_n$ (III) was carried out by a procedure similar to that used for **I** starting from equimolar amounts of $Pd_3(CH_3CO_2)_6$ (0.224 g, 1 mmol) and fumaric acid (0.116 g, 1 mmol) in CH_3OH until a light brown precipitate formed. The product yield was 45%.

For $C_4H_6O_6Pd$		
Anal. calcd., %	C, 18.65	H, 2.74
Found, %	C, 19.04	H, 2.88

Synthesis of $[Pd(HOOC{-}CH{-}CH(CH_3O))(CH_3CN)_2]$ (IV). Maleic acid (0.116 g, 1 mmol) and CH_3CN (5 mL) were added into the mother liquor formed after separation of the precipitate in the synthesis of **I**. The color of the reaction mixture changed from light brown to light green. After 5 days, a light green solid (with microinclusions of Pd metal) precipitated; a single crystal was selected from the precipitate.

Elemental analysis was carried out on a CHNSOEA 1108 (Carlo Erba Instruments) analyzer.

The IR spectra of the crystalline samples were measured in the 4000–550 cm^{-1} range in the ATR mode on a NEXUS (NICOLET) FTIR spectrometer (single-beam scanning spectrometer, CsI beam splitter, TGS-CsI detector, photometric accuracy of 0.1%, and resolution of 2 cm^{-1}) using a MIRacle attachment (PIKETechnologies) with a diamond crystal. The samples were applied directly on the diamond crystal without special preparation.

Raman spectra were measured using an in Via Renishaw Raman spectrometer with the laser radiation wavelength $\lambda = 633$ nm and a power below 1 mW.

The ESR spectra of the complexes were recorded on an Elexsys E680X BRUKER ESR spectrometer in the X-range (operating frequency of ~9.8 Hz) at room temperature. After the synthesis, the products were placed into quartz tubes and stored in the tubes throughout the experiments. Heating to 40°C was carried out directly in the tubes. The spectra of the test compounds were corrected to the spectrum of the empty cavity. The concentration of unpaired electrons was determined by double integration of the ESR spectra and subsequent analysis of the results by the SpinCount function of the ESR spectrometer, which was calibrated against the Alanine Spin Concentration Sample (BRUKER) with a concentration of unpaired electrons of 1.75×10^{17} (±10%).

The differential thermal analysis was performed on an SDT Q600 synchronous thermal analyzer (TA Instruments) under isothermal conditions at 40°C and with temperature ramping in the 25–250°C range at a rate of 5°C/min.

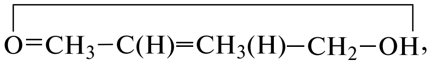
X-ray diffraction study of **IV** was carried out on a Bruker SMART APEX II automated diffractometer at 240 K (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). The absorption correction was applied using measured intensities of equivalent reflections [33, 34]. The structure was solved by direct methods; all non-hydrogen atoms were refined by the full-matrix anisotropic least squares method on F^2 (SHELXTL) [33]. All hydrogen atoms were placed into calculated positions and refined using the riding model. The crystal was a racemic twin with 0.56(5) : 0.44(5) component ratio.

The crystal structure parameters of **IV** were deposited with the Cambridge Crystallographic Data Centre (CCDC) (no. 2039147; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The Pd(I) polymeric complexes $\{[cis\text{-}Pd(C_4H_2O_4)(H_2O)]\cdot(H_2O)\}_n$ (**I**), $\{[cis\text{-}Pd(C_5H_4O_4)(H_2O)]\cdot 2H_2O\}_n$ (**II**), and $\{[trans\text{-}Pd(C_4H_2O_4)(H_2O)]\cdot(H_2O)\}_n$ (**III**) were prepared here by reactions of Pd(II) acetate with maleic, citraconic, or fumaric acid in 1 : 1 ratio in methanol. The reaction was accompanied by the reduction of Pd(II) and gave Pd(I) coordination polymers. According to analytical data, the obtained compounds were characterized by the Pd : dicarboxylate ion : H_2O ratio of 1 : 1 : $(H_2O)_n$, where $n = 2$ (**I**, **III**) and 3 (**II**), and were almost insoluble in standard organic solvents.

The structures of **I**–**III** are determined, first of all, by the structure of the initial acid (Scheme 1), particularly, by the positions of the carboxylate groups relative to the double bond: *cis*-position in maleic and citraconic acids and *trans*-position in fumaric acid. Analysis of the structural data for maleic and fumaric acids by quantum chemistry methods allowed Macoas et al. [35] to identify the most stable conformers of maleic and fumaric acids. The most stable, nearly planar conformer of maleic acid contains the seven-membered ring



$\overline{O{=}CH_3{-}C(H){=}CH_3(H){-}CH_2{-}OH}$,

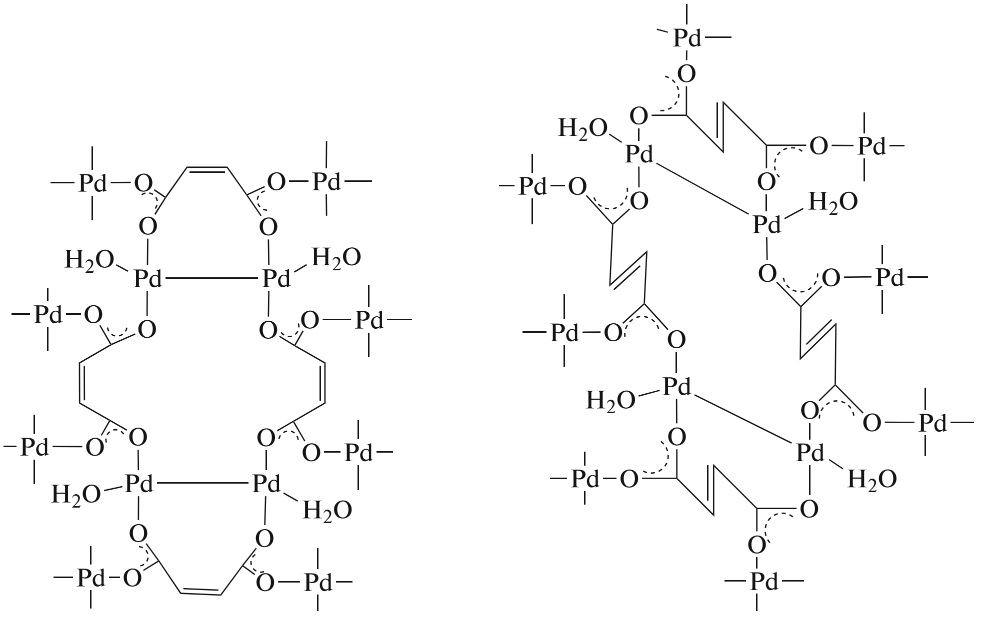
which is formed via the –OH...O=C– intramolecular hydrogen bond between the carboxylate groups of one maleic acid molecule [35]. The results were confirmed by simulated and experimental IR spectra, namely, the positions of non-conjugated and conjugated OH and CO groups. While considering the data for fumaric acid, Macoas et al. [35] identified three most stable conformers with slightly differing IR spectra, representing broad bands in the 1760–1765 cm^{-1} range, which is due to strong conjugation of the carboxylate groups located in the *trans*-positions relative to the double bond in fumaric acid.

It is noteworthy that IR spectroscopy studies reported in [35] were carried out at liquid nitrogen temperature using high-purity samples of monomeric acids prepared by a special procedure. The acids used in our study were not specially purified. Some deviations between the positions of IR spectral bands of the acids used in this study and those observed previously [35] are due to difference between the methods of recording the spectra and sample preparation. Nevertheless, IR spectroscopic characteristics of the acids we used did not differ basically from the data reported earlier [35]. Thus the existence of a seven-membered ring in the maleic acid used in this work is confirmed by the bands for exocyclic and endocyclic C=O groups at 1812 and 1703 cm^{-1}, similar to the bands for these groups at 1808 and 1722 cm^{-1} reported in [35], and by appearance of bands at 2164 and 1887 cm^{-1}, attributable to the hydrogen bond forming the seven-membered ring in maleic acid. The complex system of C=C and C=O conjugated bonds of the acyclic fumaric acid molecule is manifested as a broad IR band at 1691 cm^{-1}, in which separate C=C and C=O modes cannot be distinguished. The spectrum of the citraconic acid (CH_3 group at the double bond instead of a proton) exhibits the ν(C=O) mode at 1691 cm^{-1} and the ν(C=C) mode at 1640 cm^{-1}. The spectra of maleic, citraconic, and fumaric acids show a broad absorption region with several bands in the 3100–2100 cm^{-1} range, characterizing the formation of intra- and intermolecular hydrogen bonds. Against the broad absorption background, the spectrum shows peaks at

3057 **(I)**, 3060 (**II**), and 3082 (**III**), corresponding to the ν(CH) stretching mode, and at 2994, 2961 cm^{-1} (**II**), corresponding to the ν(CH_3) mode. The δ(COH) and ν(COH) bands typical of carboxylic acids are manifested in the ranges of 1450–1420 and 1300–1200 cm^{-1}, respectively, characteristic of this class of compounds. This detailed analysis of the spectra of the acids we used, considering also reported data [35], was necessary to identify the changes in the IR spectra of the carboxylate groups upon the coordination to palladium.

The spectra of **I**–**III** no longer contain bands for conjugated and non-conjugated OH and C=O groups of the acids, but instead they exhibit ν_{as}(COO) bands at 1555 (**I**), 1539 (**II**), and 1516 (**III**) cm^{-1} and ν_s(COO) bands at 1382 (**I**), 1374 (**II**), and 1383 cm^{-1} (**III**). This set of bands attests to a bridging coordination of the carboxylate groups of both acids. In **I**–**III**, with the Pd : dicarboxylate ion ratio of 1 : 1 being retained, each palladium atom coordinates only one oxygen atom of one dicarboxylic acid carboxylate group, while the second oxygen atom of each bridging carboxylate group is coordinated to the nearest palladium atom of the neighboring cluster. Thus, one dicarboxylic acid molecule links together four palladium atoms, thus forming a polymer network with bulky cavities (pores). This is manifested as broadening of bands corresponding to the ν_{as} modes and is observed only in the IR spectra of **I**–**III**.

The presence of water molecules in **I**–**III** is reflected in the IR spectra as a broad band corresponding to ν(OH) modes in the 3300–3200 cm^{-1} range [21]. The δ(HOH) bands of **I**–**III** are superimposed by the ν_{as}(COO) modes of these complexes. The coordination sphere of each Pd(I) atom is completed by one coordinated water molecule and the Pd–Pd bond; the presence of this bond is evidenced by a band at 306 cm^{-1} corresponding to the ν(Pd–Pd) mode in the Raman spectrum. In view of the foregoing and X-ray diffraction data for Ag(I) maleate and fumarate polymer matrices, which are based on binuclear Ag(I) maleate and tetranuclear Ag(I) fumarate [23], it was concluded that a tetranuclear cluster is the building block of coordination polymers **I**–**III**. Each dicarboxylic acid molecule links four palladium atoms, which accounts for the formation of the polymer network of **I**–**III**. As can be seen in Scheme 2, the frameworks of clusters **I** and **III** are structurally similar; however, due to different orientations of the carboxylate groups in maleic (*cis*-arrangement in **I**) and fumaric acids (*trans*-arrangement in **III**), the coordination polymers should be formed by cluster units with different pore sizes.



(I) **(III)**

Scheme 2.

It is known that ESR spectroscopy is an extremely sensitive method for detecting unpaired electrons in compounds and materials of various nature, in particular in coordination compounds [36]. Figure 1 shows the ESR spectra of **I**–**III** at room temperature, similar to the spectra of Pd(I) complexes with sorbic and 4-pentenoic acids [29]. The presence of unpaired electrons in compounds **I**–**III**, according to ESR data, indicates that at the time of complex isolation, the formation of the Pd—Pd bond in their polymer matrix has not been completed, but it slows down in the solid-phase matrix upon the isolation of complexes **I**—**III**.

By measuring the concentration of unpaired electrons, it is possible to elucidate the effect of the nature of the carboxylate ligand on the formation of paramagnetic centers in the polymer matrix. It can be seen in Table 1 that their concentration is nearly the same for **I** and **II** with *cis*-arranged carboxylate groups and is almost an order of magnitude higher for **III** in which the carboxylate groups are in *trans*-positions.

The number of paramagnetic centers in polymer matrices **I**—**III** can be affected by conditions of their synthesis. For example, the replacement of methanol by acetone in the synthesis of Pd(I) citraconate (**II**) increases the number of unpaired electrons to 2.45×10^{18} spin/g versus 2.46×10^{17} spin/g for the synthesis of **II** in methanol. A decrease in the temperature of synthesis of **I** is accompanied by increase in the number of unpaired electrons in the sample up to 1.05×10^{19} spin/g in comparison with their content in **I** synthesized at room temperature (2.52×10^{17} spin/g). The above results on the increase in the number of unpaired electrons upon replacement of methanol by acetone or upon lowering of reaction temperature indicate that the formation of Pd—Pd bond is retarded in the polymer matrix of **I** and under the described conditions of the synthesis of **II**, while the gross formula is retained. Therefore, it is of obvious interest to study the effect of temperature rise on the processes taking place in the polymer matrices of compounds **I**—**III**.

Data on the processes occurring in **I**—**III** during heating were obtained by TG and DTA. First, we studied the weight changes taking place for compounds **I**—**III** under isothermal conditions at 40°C (2 h) and the accompanying changes in the concentrations of unpaired electrons. Complexes **I** and **III** lose 6% of their weight, which is somewhat smaller than the loss of one solvation water molecule per Pd atom (7%), as holding at 40°C is stopped after 2 h. The thermogram of **II**, recorded under the same conditions, shows the weight loss of 12%, which corresponds to elimination of two solvation water molecules.

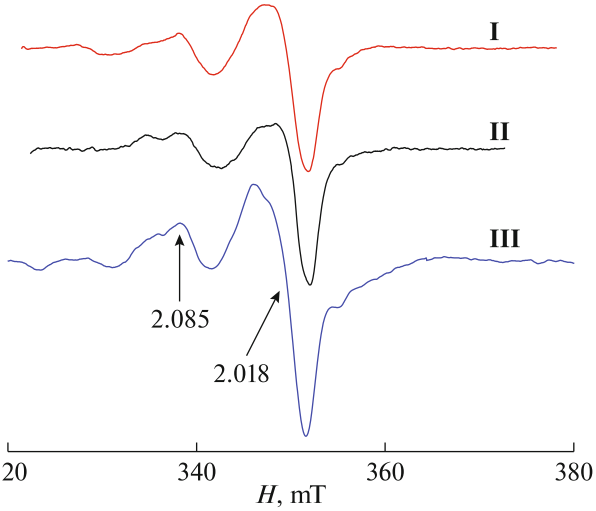


Fig. 1. ESR spectra of complexes **I**—**III** at room temperature.

According to ESR spectroscopy data, the isothermal holding of **I**—**III** (40°C, 2 h) and the subsequent storage of the samples at room temperature for 4 months result in some decrease in the concentration of unpaired electrons in their polymer matrices (Table 1). Although this attests that the slow formation of Pd—Pd bonds is continued, the obtained Pd(I) polymeric dicarboxylates can be classified as coordination polymers with stable paramagnetic centers.

The thermograms obtained by heating of **I**—**III** in the range of 30—250°C at a rate of 5°C/min represent smooth differential curves, in which the 35—50°C range corresponds to the loss of one solvation water molecule. At 90°C, an endothermic process takes place, accompanied by a weight loss higher than the loss of only solvation water molecules (7%) and corresponding to the onset of removal of coordinated water molecule. However, above 100°C, the endothermic process smoothly turns into the exothermic decomposition of the whole complex, which ends at 135—150°C. The weight of the solid residue corresponds to the Pd content in the starting complexes **I** and **III** (41%). The thermogram of **II** shows a weight loss of ~12%, corresponding to elimination of two solvation water molecules. Then, a sharp weight loss of ~63% takes place in the 150—175°C range, indicating decomposition of the whole complex.

Table 1. Concentration of unpaired electrons in the polymer matrix of **I**—**III** according to ESR data

Compound	Concentration of unpaired electrons, spin/g		
	after the synthesis	after 2 h at 40°C	after storage for 4 months
I	2.52×10^{17}	1.57×10^{17}	1.08×10^{17}
II	2.46×10^{17}	1.18×10^{17}	5.02×10^{16}
III	1.75×10^{18}	1.16×10^{18}	8.74×10^{17}

Table 2. Crystallographic data and structure refinement details for **IV**

Parameter	Value
Molecular formula	$C_9H_{12}N_2O_5Pd$
M	334.61
Crystal size, mm	0.40 × 0.20 × 0.20
System	Orthorhombic
Space group	$Pna2_1$
a, Å	13.3046(4)
b, Å	14.3496(4)
c, Å	12.7197(3)
V, Å^3	2428.39(11)
Z	8
ρ(calcd.), g/cm^3	1.830
$\mu(\mathrm{Mo}K_\alpha)$, mm^{-1}	1.539
$F(000)$	1328
θ Range, deg	2.09–30.00
Ranges of indices	$-18 \le h \le 18$, $-19 \le k \le 20$, $-17 \le l \le 16$
Total number of reflections	27856
Number of unique reflections (R_{int})	6400 (0.0321)
Number of reflections with $I > 2\sigma(I)$	5670
Number of refined parameters	314
R_1 for $I > 2\sigma(I)$	0.0588
wR_2 (all data)	0.1452
GOOF on F^2	1.125
$\Delta\rho_{min}/\Delta\rho_{max}$, e/Å^3	–0.584/3.394

As it was shown previously [29], removal of the coordinated water molecule from the coordination sphere of Pd(I) monocarboxylate (sorbate) is accompanied by conversion of the complex into diamagnetic one. However, as shown by the study of Pd(I) dicarboxylates, the removal of the coordinated water molecule from **I**–**III** is accompanied by decomposition of the whole complexes, which rules out the possibility of obtaining anhydrous diamagnetic analogues, such as Pd(I) sorbate [29].

A dependence of the reactivity of compounds **I**–**III** on the nature of carboxylic acids that form the complexes was demonstrated by performing reactions of **I**–**III** with CH_3CN. Upon the reaction of complex **III** with CH_3CN, palladium is rapidly reduced to Pd(0) both in methanol and in acetone. Complex **II** is reduced in the reaction with CH_3CN if the reaction is carried out in methanol. Complex **I** reacts with CH_3CN to be reduced to Pd(0) in acetone, while the reaction in methanol affords a mononuclear Pd(II) complex, $[Pd(HOOC–CH–CH(CH_3O))(CH_3CN)_2]$ (**IV**), the structure of which is supported by X-ray diffraction data (Fig. 2). Complex **IV** is formed as a result of two reactions. The first one is the redox reaction in which Pd(I) in the starting complex disproportionates to the Pd(II) complex and Pd(0), which is present as microinclusions in the crystal mass of complex **IV**. The second reaction, reduction of the double bond to a single bond, is accompanied by the formation of a five-membered ring linked to Pd(II) via the β-carbon atom of the reduced double bond and via oxygen of one carboxylate group of maleic acid. The second protonated carboxylate group remains free. The Pd(II) coordination sphere is completed by two acetonitrile molecules. Tables 2 and 3 summarize the crystallographic data for **IV**.

The pseudo-symmetric structure of **IV** contains two crystallographically independent molecules with very similar geometric parameters, as evidenced by the result of the superposition of the molecules using the least squares method (Fig. 3).

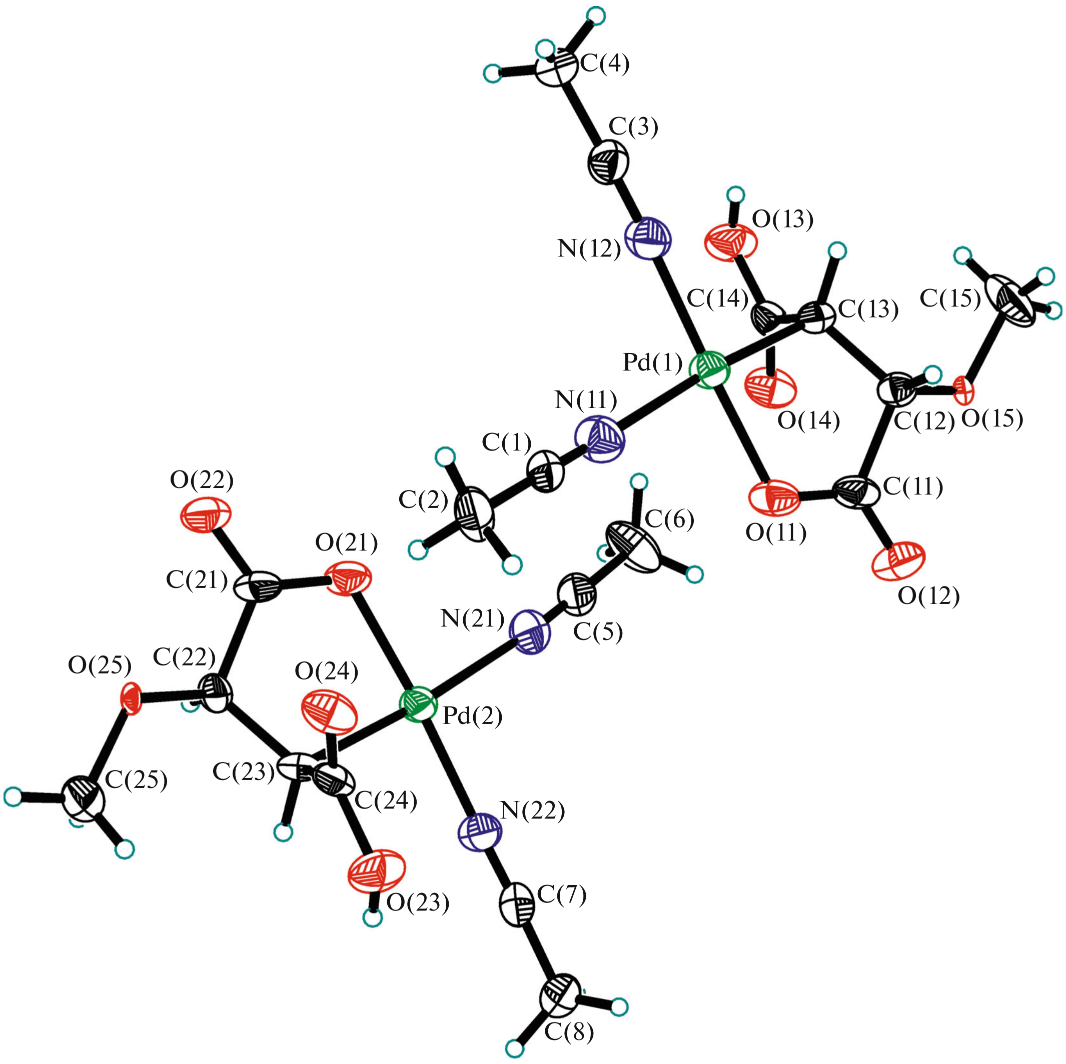


Fig. 2. Both crystallographically independent molecules in **IV**. Thermal ellipsoids are drawn at 50% probability level.

The central palladium atoms are located in the square planar environment with *cis*-angles between the ligands being in the 83.44(17)°–93.6(2)° range. As was to be expected, the smallest values of these angles refer to endocyclic OPdC. The deviations of Pd atoms from the plane through the four base atoms do not exceed 0.02 Å. The coordination environment of the metal atoms is composed of a chelating O,C-ligand and two acetonitrile molecules located in *cis*-positions relative to each other. It is worth noting that the Pd–N distances in the two molecules differ by more than 0.1 Å, which is apparently caused by markedly different *trans*-effects of the opposing ligands. The Pd–O bond lengths are close to the average value found for non-bridged palladium carboxylate complexes present in the CCDC [37]—2.043 Å (876 structures, version 5.40, August 2019). The same is true for the Pd–C_{Alk} bond, for which the average length found among the square planar palladium complexes is 2.057 Å, according to CCDC data (over 1487 structures). In both molecules, the five-membered metallacycle has the envelope conformation in which the C(13) and C(23) carbon atoms bound to the metal form the flap. In the crystal, neighboring molecules are connected in

Table 3. Bond lengths (*d*) in compound **IV**

Bond	Bond length, Å
Pd(1)–N(12)	1.974(5)
Pd(2)–N(22)	1.981(4)
Pd(1)–O(11)	1.995(4)
Pd(2)–O(21)	2.000(4)
Pd(1)–C(13)	2.043(5)
Pd(2)–C(23)	2.030(5)
Pd(1)–N(11)	2.115(5)
Pd(2)–N(21)	2.122(5)

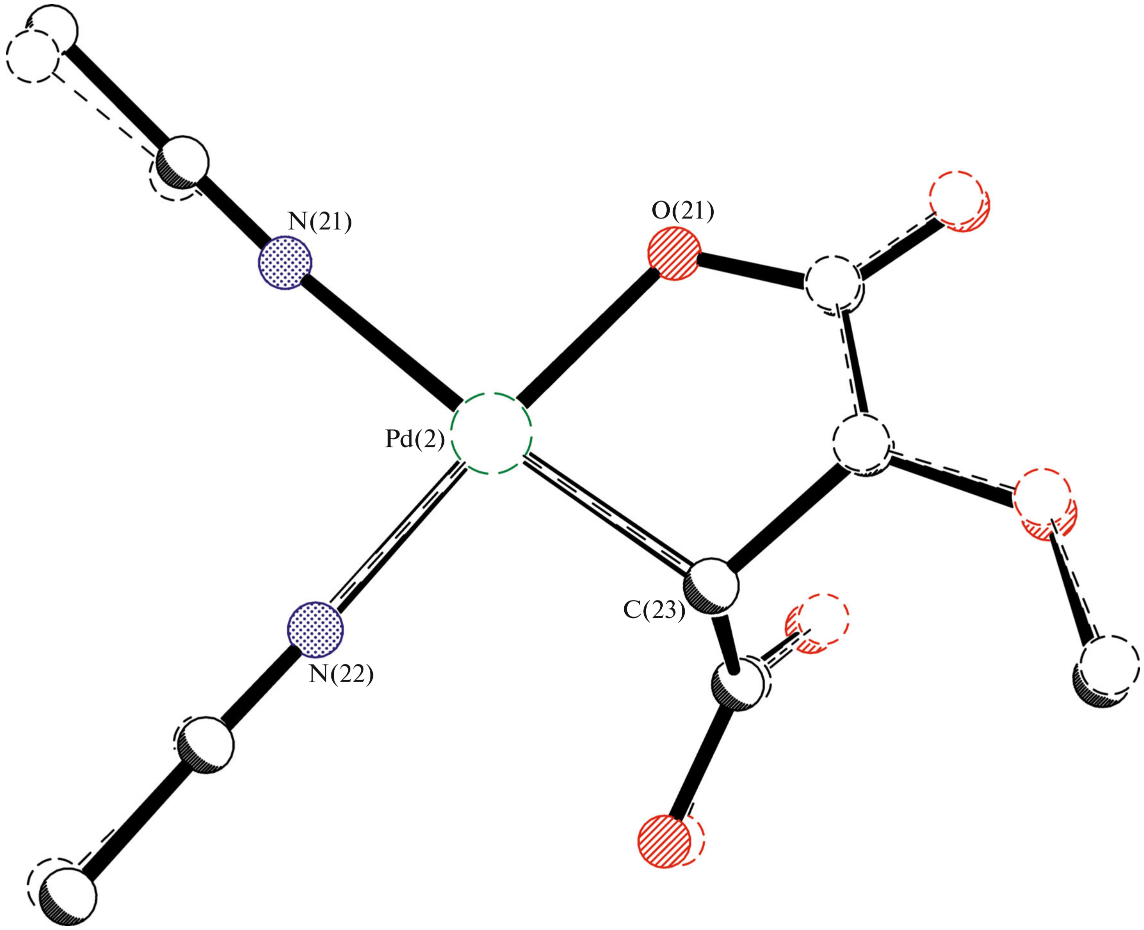


Fig. 3. Superimposition of independent molecules in **IV** by the least-squares method.

chains along the *a* axis via strong hydrogen bonds (O...O, 2.649(7), 2.652(7) Å) between the carboxyl groups (Fig. 4).

Thus, we performed the first synthesis of Pd(I) coordination polymers with unsaturated dicarboxylic acids, namely, maleic, citraconic, and fumaric acids, containing stable paramagnetic centers in their polymer matrix. According to IR and ESR spectroscopy and thermogravimetric data, probable building blocks forming complexes **I**–**III** are clusters whose cage consists of four palladium atoms, which coordinate four acid molecules. The coordination sphere of each Pd(I) atom is completed by one water molecule and the Pd–Pd bond. When compounds **I**–**III** are kept at 40°C, only solvation water molecules are lost. When the thermogravimetric curves of **I**–**III** are recorded in the 30–250°C range, the loss of solvation water molecules is followed by elimination of coordination water molecules, which is accompanied by complete reduction of palladium to $\mathrm{Pd_{met.}}$

When **I** reacts with CH_3CN in methanol, the redox reaction is accompanied by disproportionation of **I** to give Pd(II) complex and Pd(0). In the resulting complex $[\mathrm{Pd(HOOC{-}CH{-}CH(CH_3O))(CH_3CN)_2}]$ (**IV**), the Pd(II) coordination sphere is formed via coordination of two CH_3CN molecules and a five-membered ring formed after reduction of the double bond, which is bound to Pd(II) via the Pd–β-C bond and the oxygen atom of one carboxylate group of maleic acid.

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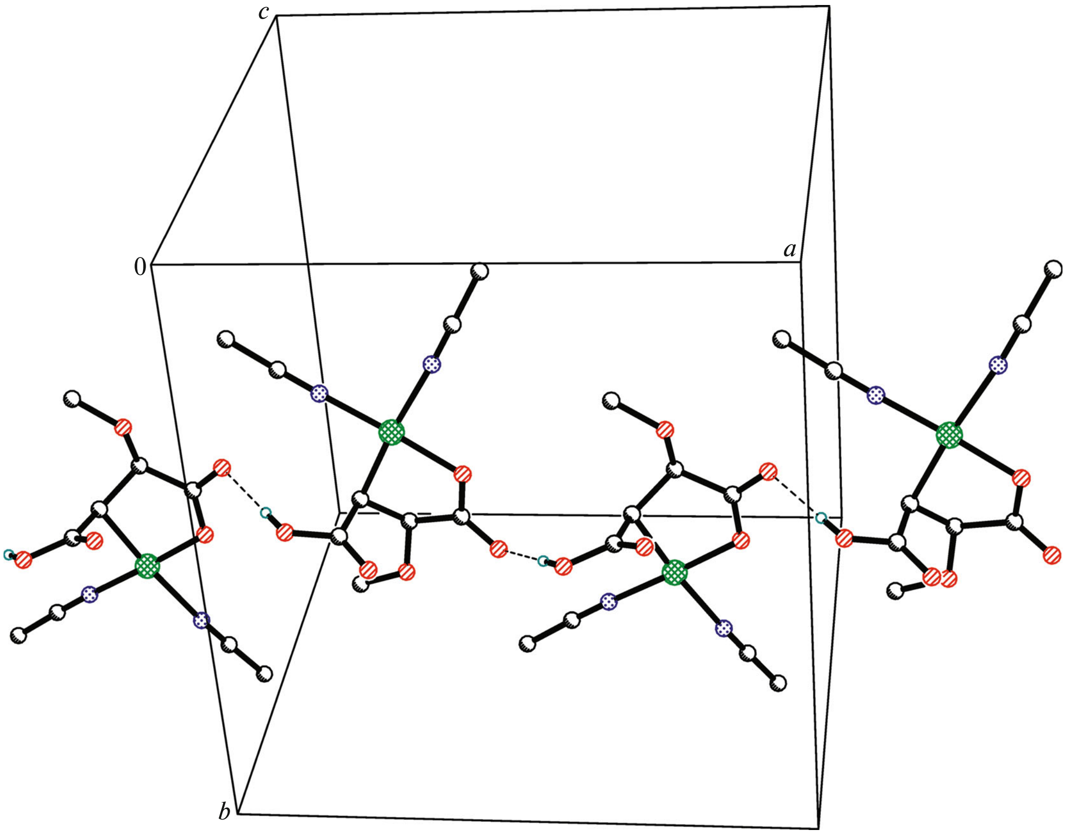

Fig. 4. Hydrogen-bonded chains of molecules in **IV**.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Bailar, J.C., *J.R.J. Inorg. React.*, 1964, vol. 1, p. 1.
2. Robin, A.Y. and Fromm, K.M., *Coord. Chem. Rev.*, 2006, vol. 250, p. 2127.
3. Noro, S.-I., Miyasaka, H., Kitagawa, S., et al., *Inorg. Chem.*, 2005, vol. 44, p. 133.
4. Zaworotko, M.J., *Chem. Soc. Rev.*, 1994, p. 283.
5. Robson, R.J., *Dalton Trans.*, 2000, p. 3735.
6. Moulton, B. and Zaworotko, M.J., *Chem. Rev.*, 2001, vol. 101, p. 1629.
7. Kim, K., *Chem. Soc. Rev.*, 2002, vol. 31, p. 96.
8. Miyasaka, H., Matsumoto, N., Okawa, H., et al., *J. Am. Che. Soc.*, 1996, vol. 118, p. 981.
9. Coronado, E., Gaslan-Mascaros, J.R., Gomez-Garcia, C.J., et al., *Nature*, 2000, vol. 408, p. 447.
10. Hunig, S., Kemmer, M., Meixner, H., et al., *Eur. J. Inorg. Chem.*, 1999, p. 899.
11. Kitagawa, H., Onodera, N., Sonoyama, T., et al., *J. Am. Chem. Soc.*, 1999, vol. 121, p. 10068.
12. Hou, H., Meng, X., Song, Y., et al., *Inorg. Chem.*, 2002, vol. 41, p. 4068.
13. Barthelet, K., Marrot, J., Riou, D., et al., *Angew. Chem., Int. Ed. Engl.*, 2002, vol. 41, p. 281.
14. Kim, J., Chen, B., Reinkek, T.M., et al., *J. Am. Chem. Soc.*, 2001, vol. 123, p. 8239.
15. Dzhardimalieva, G.I. and Pomogailo, A.D., *Usp. Khim.*, 2008, vol. 77, no. 3, p. 270.
16. Kickelbick, G., *Prog. Polym. Sci.*, 2003, vol. 28, no. 1, p. 83.
17. Pomogailo, A.D. and Savostyanov, V.S., *Synthesis and Polymerization of Metal-Containing Monomers*, BocaRaton(FL): CRCPress, 1994.
18. Porai-Koshits, M.A., *Itogi Nauki i Tekhniki, Kristallokhimiya*, 1981, vol. 1, p. 3.
19. Pisarevskii, A.P. and Martynenko, L.I., *Koord. Khim.*, 1994, vol. 20, p. 324.
20. Kiskin, M.A. and Eremenko, I.L., *Usp. Khim.*, 2006, vol. 75, p. 627.
21. Porollo, N.P., Aliev, Z.G., Dzhardimalieva, G.I., et al., *Russ. Chem. Bull.*, 1997, vol. 46, no. 2, p. 362.
22. Mori, W. and Takamizawa, S., *J. Solid State Chem.*, 2000, vol. 152, p. 120.
23. Mori, W., Sato, T., Ohmura, T., et al., *J. Solid State Chem.*, 2005, vol. 178, p. 2552.
24. Bar, A.K., Chakrabarty, R., and Mukherjee, P.T., *Organometallics*, 2008, vol. 27, p. 3806.
25. Neo, Y.C., Yeo, J.S.L., Low, P.M.N., et al., *J. Organomet. Chem.*, 2002, vol. 658, p. 159.

26. Fernandes, R.L., Takashi, P.M., Frem, R.C.G., et al., *J. Term. Analit. Calorim.*, 2009, vol. 97, p. 153.
27. Efimenko, I.A., Ankudinova, P.V., Kuz'mina, L.G., et al., *Russ. J. Inorg. Chem.*, 2015, vol. 6, no. 7, p. 848. https://doi.org/10.1134/S0036023615070050
28. Efimenko, I.A., Demina, L.I., Ankudinova, P.V., et al., *Russ. J. Inorg. Chem.*, 2016, vol. 61, no. 10, p. 1252. https://doi.org/10.1134/S0036023616100090
29. Efimenko, I.A., Erofeeva, O.S., Ugolkova, E.A., et al., *Mend. Commun.*, 2018, vol. 28, p. 632.
30. Prakash, A.M., Wasowicz, T., and Kevan, L., *J. Phys. Chem.*, 1997, vol. 101, p. 1985.
31. Stokes, L.S., Murphy, D.M., Farley, R.D., et al., *Phys. Chem. Chem. Phys.*, 1999, vol. 1, p. 621.
32. Ghosh, A.K. and Kevan, L., *J. Am. Chem. Soc.*, 1988, vol. 110, p. 8044.
33. Sheldrick, G.M., *SADABS. Program for Scaling and Correction of Area Detector Data*, Göttingen: Univ. of Göttingen, 1997.
34. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112.
35. Macoas, E.M.S., Fausto, R., Lundell, J., et al., *J. Phys. Chem. A*, 2001, vol. 105, p. 3922.
36. Rakitin, Yu.V., Larin, G.M., and Minin, V.V. *Interpretatsiya spektrov EPR koordinatsionnykh soedinenii* (Interpretation of ESR spectra of Coordination Compounds), Moscow: Nauka, 1993.
37. Groom, C.R., Bruno, I.J., Lightfoot, M.P., et al., *Acta Crystallogr., Sect. B: Found. Adv.*, 2016, vol. 72, p. 171.

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