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Paramagnetic Pd^+ centers in the polymeric matrices of palladium(I) sorbates and 4-pentenate

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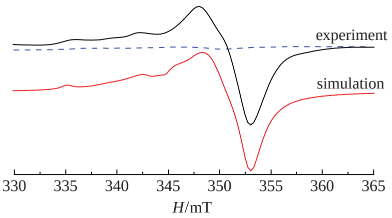
The paramagnetic Pd^I centers with unpaired electrons have been first revealed by EPR spectroscopy in the polymeric matrices of Pd^I sorbates $[Pd(C_6H_7O_2)H_2O]_n$, $[Pd(C_6H_7O_2)]_n$ and 4-pentenate $[Pd(C_5H_7O_2)H_2O]_n$. These compounds have been obtained by the reactions between $Pd_3(MeCO_2)_6$ and sorbic (MeCH=CHCH=CHCOOH) and 4-pentenoic (CH_2=$CHCH_2CH_2COOH$) acids in MeOH.



Organopalladium(I) complexes have attracted wide attention since 1942 when Gel'man and Meilakh[1] synthesized first dipalladium(I) complexes in a reaction between $[PdCl_4]^{2-}$ and CO in aqueous HCl. Many publications[2–7] were devoted to the structures, coordination behaviors, reactivity, and functions of organopalladium(I) complexes containing Pd–Pd bonds. The possibility to produce palladium(I) with unpaired electrons by the irradiation of diamagnetic Pd^{II} compounds with γ-rays or high energy electrons was shown in early EPR studies.[8–10] CW and pulse EPR spectroscopy was used for studying paramagnetic Pd ions in solid matrices.[11–15] The preparation and characterization of paramagnetic palladium(I) complexes were reported.[16] One of the test complexes exhibited EPR signals only at low temperatures (~20 K) and became EPR-silent at temperatures higher than 77 K, but another Pd^I complex with thiophosphoryl thiocarbamide stabilizer has strong EPR signals at room temperature without any activation or irradiation.

In this work we prepared and investigated insoluble polymeric palladium carboxylates. They were synthesized by reactions of $Pd_3(MeCO_2)_6$ with sorbic acid and 4-pentenoic acid in MeOH. According to elemental analysis data, the Pd : carboxylate ratio was 1 : 1; therefore, the general formulas of the compounds synthesized were $[Pd(C_6H_7O_2)H_2O]_n$ **1**, $[Pd(C_6H_7O_2)]_n$ **1a**, and $[Pd(C_5H_7O_2)H_2O]_n$ **2**.[†] The composition corresponds to a formal palladium oxidation state of 1+. Complex **1a** is the first binary palladium(I) complex with unsaturated acids. The palladium(I) sorbates and 4-pentenate **1**, **1a**, **2** are believed to be diamagnetic. EPR spectroscopy[‡] was used to determine Pd^I unpaired electrons in complexes **1**, **1a**, and **2**. Complex **1a** was found to be diamagnetic. To the best of our knowledge, no palladium(I) carboxylates having Pd^I atoms with an unpaired electron have been described so far. Figure 1 shows the EPR spectra of compounds **1** and **2**. An intense signal is observed at $g = 2$ ($H = 350$ mT). The EPR spectrum of complex **1** is described by a rhombically distorted spin Hamiltonian (SH).[§] The best agreement between the experimental and theoretical spectra[17–19] was obtained for the following SH parameters: $g_z = 2.042$, $g_x = 2.018$, $g_y = 2.000$, $a = 3.97\times10^{-3}$ cm^{-1}, $b = 1.79\times10^{-3}$ cm^{-1}, and $c = 3.60\times10^{-3}$ cm^{-1}. The presence of a hyperfine structure (HFS) because of the magnetic interaction of an unpaired electron with ^{105}Pd nuclei (natural abundance, 22%; $I = 5/2$) in the parallel orientation of the g-tensor and the ratio $g_z > g_y$ allowed us to assert that the resulting spectrum of compound **1** is that of the Pd^I complex bearing an unpaired

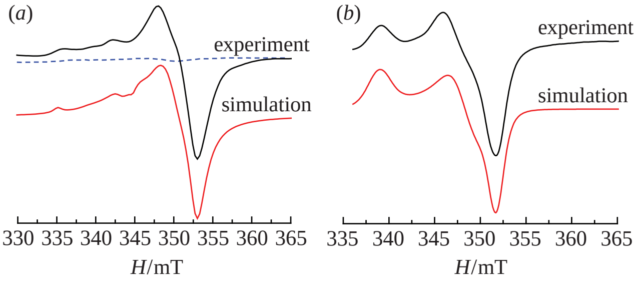


Figure 1 Experimental and theoretical EPR spectra of polymeric compounds (*a*) **1** and (*b*) **2** at $T = 293$ K. The EPR spectrum of complex **1a** is shown by a dotted line.

[†] *Synthesis of $[Pd(C_6H_7O_2)H_2O]_n$* **1**. A round bottom flask was charged with a solution of $Pd_3(MeCO_2)_6$ (0.224 g, 1 mmol) in MeOH and sorbic acid (0.168 or 0.224 g, 1.5 or 2 mmol). The resulting solution was stirred at 20–25°C for 24 h to form an orange precipitate, which was filtered off using a Shott filter no. 16, washed with methanol (3×10 ml), and dried in a vacuum. Yield, 30%. Found (%): C, 30.11; H, 3.65. Calc. for $PdC_6H_9O_3$ (%): C, 30.64; H, 3.83. IR (ν/cm^{-1}): 1556 (ν_{as}), 1377 (ν_s), $\Delta\nu = 179$.

Synthesis of $[Pd(C_6H_7O_2)]_n$ **1a**. The reaction was carried out according to the above procedure using the equimolar amounts of $Pd_3(MeCO_2)_6$ (0.224 g, 1 mmol) and sorbic acid (0.112 g, 1 mmol). Yield, 45%. Found (%): C, 32.52; H, 4.23. Calc. for $PdC_6H_7O_2$ (%): C, 33.12; H, 3.24. IR (ν/cm^{-1}): 1555 (ν_{as}), 1390 (ν_s), $\Delta\nu = 165$.

Synthesis of $[Pd(C_5H_7O_2)H_2O]_n$ **2**. The reaction was carried out analogously using the equimolar amounts of $Pd_3(MeCO_2)_6$ (0.224 g, 1 mmol) and 4-pentenoic acid (0.100 ml, 1 mmol). Yield, 70%. Found (%): C, 27.06; H, 3.59. Calc. for $PdC_5H_9O_3$ (%): C, 26.91; H, 4.04. IR (ν/cm^{-1}): 1565 (ν_{as}), 1390 (ν_s), $\Delta\nu = 175$.

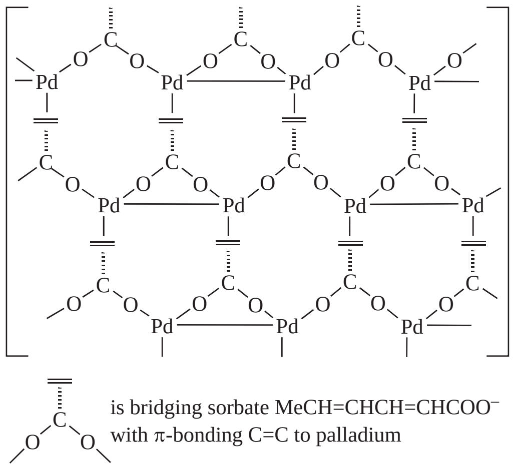
[‡] The EPR spectra were recorded on a Bruker Elexsys E680 XEPR spectrometer in the X-band (frequency, ~9.8 GHz) at room temperature.

[§] $H = g_z\beta H_z S_z + g_x\beta H_x S_x + g_y\beta H_y S_y + aI_zS_z + bI_xS_x + cI_yS_y$.

electron. The spectrum is characteristic of the paramagnetic Pd^I center with the ground state of the central atom to be $|x^2 - y^2\rangle$, which is confirmed by the agreement between the experimental and theoretical spectra [Figure 1(*a*)].

In the EPR spectrum of complex **2** [Figure 1(*b*)], there is no HFS resulted from the ^{105}Pd nuclei, which is explained by strong magnetic interactions between paramagnetic centers leading to a broadened spectrum line. For complex **2**, the best agreement between the experimental and theoretical spectra was obtained for $g_z = 2.083$, $g_x = 2.028$, and $g_y = 2.008$. The absence of signals from the EPR spectrum of **1a** indicates that the Pd–Pd bond exists and **1a** is diamagnetic because of coupling unpaired electrons from two nearest Pd^I atoms [the dotted line in Figure 1(*a*)]. Note that, in contrast to **1a**, complexes **1** and **2** contain water molecules. In this case, the polymeric matrices of **1** and **2** are formed in two ways: by the Pd–Pd bond formation similarly to **1a** and by Pd^I coordination with the water molecules. The latter process makes difficulties in the coupling of unpaired electrons. In order to detect paramagnetism, we investigated the magnetic behaviors of **1** and **2**.[¶] Despite the presence of a sufficiently strong signal in the EPR spectrum, both complexes were found diamagnetic at 300 K. Thus, the diamagnetic contribution of the compounds significantly exceeds the paramagnetic one. Thus, we can conclude that the concentration of Pd^I ions in the compounds is small. These results indicate the presence of Pd–Pd bonds in complexes **1** and **2**.

The structures of **1**, **1a** and **2** were analyzed using IR, Raman[††] and EPR spectroscopy data and magnetic data. The IR spectra of **1**, **1a** and **2** show that the stretching vibration frequencies $\nu_{as(COO)}$ (1555–1565 cm^{-1}) and $\nu_{s(COO)}$ (1377–1390 cm^{-1}) are similar to those of all of the synthesized carboxylates, and they indicate that the test carboxylates are bridging ligands. This conclusion is confirmed by the difference between ν_{as} and ν_s stretches $\Delta\nu = \nu_{as} - \nu_s$ for **1**, **1a** and **2** in a range from 165 to 175 cm^{-1}.[20,21] The bases for the polymeric complexes are the building blocks $[Pd(C_6H_7O_2)]$ and $[Pd(C_5H_7O_2)]$. Two Pd^I atoms in **1**, **1a** and **2** are bound only by one bridging carboxylate fragment forming the chains of infinite extent $[–Pd–OC(R)O–Pd–OC(R)O–Pd–]_n$ opposed to the palladium(II) carboxylates, where every two palladium atoms are linked together by two bridging carboxylates.[22,23] The broadening of the $\nu_{as(CO_2)}$ band observed in the spectra of **1**, **1a** and **2** can be due to different carboxylate groups in these complexes. Only some of them are opposite to the Pd–Pd bonds. In the IR spectra of **1** and **1a**, the $\nu_{(C=C)}$ bands of sorbic acid with maxima at 1634 and 1608 cm^{-1} are shifted to 1645 and 1615 cm^{-1}, while they are shifted to 1647 and 1618 cm^{-1}, respectively, in the Raman spectra. Small shifting of the $\nu_{(C=C)}$ band to the shorter wavelengths by ~10 cm^{-1} can be explained by the essential redistribution of both double-bond systems resulting from a modified double-bond conjugation with carboxylate when coordinating palladium(I).[24,25] In the IR spectra of **2**, the $\nu_{(C=C)}$ bands are overlies by the $\nu_{as(COO)}$ bond of 4-pentenate, while the $\nu_{(C=C)}$ band in the Raman spectra appears at significantly lower wavenumbers (1558, 1534 cm^{-1}) as compared to the $\nu_{(C=C)}$ band (1642 cm^{-1}) of 4-pentenoic acid. The results of IR spectroscopy indicate the π-bonding of C=C to palladium.[26] Broadened and low-intensity bands observed in the IR spectra of **1** and **2** at 3400–3200 cm^{-1} result from weakly coordinated water molecules. The proposed structure of compound **1a** is shown schematically in Figure 2.



is bridging sorbate MeCH=CHCH=CHCOO$^-$
with π-bonding C=C to palladium

Figure 2 Proposed structure of compound **1a**.

Thus, in polymeric matrix diamagnetic **1a** the palladium(I) coordination sphere comprises two dissimilar sorbate ions, Pd–Pd bonds and coordinated double bond of sorbate. The detection of paramagnetic and diamagnetic contributions in **1** and **2** testifies that two types of coordination centers exist in the polymeric matrix of **1** and **2**. The palladium(I) coordination spheres in diamagnetic fragments **1** and **2** are analogous to the palladium(I) coordination sphere of **1a**. In paramagnetic fragments **1** and **2**, the palladium(I) coordination sphere involves two sorbate or 4-pentenate ions, coordinated to palladium(I) double bond of sorbate or 4-pentenate and the molecules of water.

In summary, the Pd^I sorbates $[Pd(C_6H_7O_2)H_2O]_n$, $[Pd(C_6H_7O_2)]_n$ and 4-pentenate $[Pd(C_5H_7O_2)H_2O]_n$ were synthesized and characterized by elemental analysis and IR, Raman and EPR spectroscopy. The Pd^+ centers with unpaired electrons were found to exist in the polymeric matrices of **1** and **2**.

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[¶] Magnetic susceptibility measurements were performed with a Quantum Design magnetometer PPMS-9. The measurements were done in a 5000 Oe dc magnetic field at 300 K.

[††] The IR spectra in the range 4000–550 cm^{-1} were recorded on a Nicolet NEXUS IR-FT spectrophotometer equipped with a Pike single reflection diamond attenuated total reflection (ATR) sampling accessory. The Raman spectra were recorded on a Senterra Bruker spectrophotometer at 532 nm (0.2 mW) and 785 nm (1 mW).

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