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A Study of Complexation between Crystalline *trans*-[Pd(H_2O)$_2$(NO_3)$_2$] and Acetylacetone

S. P. Khranenko[a],*, P. E. Plusnin[a], L. A. Sheludyakova[a], Yu. V. Gerasimova[b], I. V. Korol'kov[a], and S. V. Korenev[a]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences, pr. akademika Lavrent'eva 3, Novosibirsk, 630090 Russia*

[b] *Institute of Chemical Biology and Basic Medicine, Siberian Division, Russian Academy of Sciences, Novosibirsk, Russia*

**E-mail: hranenko@che.nsk.su*

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Abstract—Complexation between crystalline *trans*-[Pd(H_2O)$_2$(NO_3)$_2$] and acetylacetone was studied. The complexes $Pd_2(Acac)_2(\mu\text{-}NO_3)_2$ (**I**) and $Pd_2(Acac)_2(\mu\text{-}Acac)(\mu\text{-}NO_3)$ (**II**) were obtained and examined by elemental analysis, X-ray powder diffraction analysis, differential scanning calorimetry, simultaneous thermal analysis, mass spectrometry, and vibrational spectroscopy.

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Palladium complexes occupy an important place in coordination chemistry. In the last few years, solutions of palladium nitrate have been intensively studied for isolation of crystalline phases with constant compositions [1–5]. The nitrate ion is a weak electron donor, which makes palladium(II) nitrate a convenient starting reagent for the synthesis of new complexes with desired properties and for accumulation of products employed in technological processes. To date, complexes of Pd(II) nitrate with alkali metal cations have been obtained and structurally characterized [6–8]. The crystalline phases of Pd(II) nitrates have been isolated from nitric acid solutions and examined by powder and single-crystal X-ray diffraction analysis [9, 10]. These phases have the constant composition and geometry of a complex corresponding to *trans*-[Pd(H_2O)$_2$(NO_3)$_2$]. In a closed system, the composition and structure of the complex remain unchanged for a long period of time.

In this study, we investigated reactions of crystalline *trans*-dinitratodiaquapalladium(II) and its concentrated aqueous solutions with organic ligands. For this purpose, we used the well-known system Pd(II)–acetylacetone (HAcac). Acetylacetone, which is a common organic ligand with the electron-donating oxygen atoms, reacts with Pd(II) to give the chelate complex $Pd(Acac)_2$. The structure of the complex was determined from physicochemical data and vibrational spectra [11]. In addition, being highly volatile, unreacted acetylacetone can be easily removed by keeping the reaction mixture in air at room temperature.

EXPERIMENTAL

Acetylacetone (HL) was the analytical-grade chemical. Crystalline *trans*-[Pd(H_2O)$_2$(NO_3)$_2$] was prepared as described in [9].

Palladium(II) complexes with HAcac were obtained by grinding the starting reagents with a given molar ratio in an agate mortar. To reduce the viscosity and homogenize the reaction mixture, we used a solution of HAcac in chloroform (1.944 mmol/ml). The mixture was ground for 20 min. This resulted in a color change from dark brown to yellow orange. Then the mixture was kept in air at room temperature to a constant weight. The final product was a yellow orange, fine crystalline solid.

For solutions, the reaction was carried out as follows. First, crystalline *trans*-[Pd(H_2O)$_2$(NO_3)$_2$] (0.2664 g, 1 mmol) was powdered, dissolved in distilled water (0.2 ml), and mixed with a solution of HAcac in chloroform. The mixture was vigorously stirred for 15–20 min. During the synthesis, the mixture turned from dark brown to yellow and a yellow orange solid phase separated. Then this phase was isolated and kept in air at room temperature to a constant weight. The final product was a yellow orange, fine crystalline powder.

In the synthesis, the molar ratio Pd : HAcac was varied from 1 : 1 to 1 : 4. The phases obtained were examined by chemical and elemental analyses. An analysis for C, H, and N was carried out on a Carlo Erba 1106 analyzer. The palladium content was determined by atomic absorption spectroscopy on a Hitachi Z-800 spectrometer for solid samples evaporated with HCl.

Table 1. Chemical and elemental analysis data for the reaction products obtained from crystalline *trans*-[$Pd(H_2O)_2(NO_3)_2$] and HAcac

Entry no.	Initial molar ratio Pd : HAcac	Characteristic of the phase obtained	Content, %			
			C	H	N	Pd
1	1 : 1.0	Orange, fine crystalline powder	22.1	2.3	5.7	39.9
2	1 : 1.5	Yellow orange, fine crystalline powder	30.8	3.7	2.8	37.3
3	1 : 2.0	Yellow, fine crystalline powder	31.4	3.8	2.7	37.2
4	1 : 3.0	Yellow orange, fine crystalline powder	31.8	3.9	2.3	37.4
5	1 : 3.3	Yellow orange, fine crystalline powder	32.0	3.9	2.4	37.1
6	1 : 3.6	Yellow, fine crystalline powder	39.2	4.5	0	35.1
7	1 : 4.0	Yellow, fine crystalline powder	39.4	4.7	0	35.0

Table 2. Chemical and elemental analysis data for the reaction products obtained from a freshly prepared 5.0 M aqueous solution of *trans*-[$Pd(H_2O)_2(NO_3)_2$] and HAcac

Entry no.	Initial molar ratio Pd(II) : HAcac	Characteristic of the phase obtained	Content, %			
			C	H	N	Pd
1	1 : 1.0	Orange, fine crystalline powder	22.6	2.5	5.3	39.3
2	1 : 1.5	Yellow orange, fine crystalline powder	31.3	3.6	2.5	37.2
3	1 : 2.0	Yellow orange, fine crystalline powder	32.1	3.9	2.3	37.2
4	1 : 2.5	Yellow orange, fine crystalline powder	31.8	3.7	2.6	37.1
5	1 : 3.0	Yellow, fine crystalline powder	39.1	4.5	0.1	34.8
6	1 : 3.3	Yellow, fine crystalline powder	39.3	4.6	0	35.0

The chemical and elemental analysis data for the phases obtained in the reactions with crystalline *trans*-[$Pd(H_2O)_2(NO_3)_2$] and its aqueous solution are summarized in Tables 1 and 2, respectively.

According to the elemental analysis data, the reaction product for Pd : HAcac = 1 : 1 is $Pd_2(Acac)_2(NO_3)_2$ (**I**), regardless of the synthetic method (Tables 1, 2). For $C_{10}H_{14}N_2O_{10}Pd_2$ anal. calcd. (%): C, 22.43; H, 2.02; N, 5.23; Pd, 39.77.

The formation of the complex can be described by the equation

$$\begin{aligned} &2\textit{trans}\text{-}[Pd(H_2O)_2(NO_3)_2] + 2HAcac \\ &= Pd_2(Acac)_2(NO_3)_2 + 2HNO_3 + 4H_2O. \end{aligned} \qquad (1)$$

For the molar ratio Pd : HAcac varied from 1 : 1.5 to 1 : 3.3 (Table 1) and from 1 : 1.5 to 1 : 2.5 (Table 2), the reaction product should have the formula $Pd_2(Acac)_3(NO_3)$ (**II**). For $C_{15}H_{21}NO_9Pd_2$ anal. calcd. (%): C, 31.46; H, 3.67; N, 2.45; Pd, 37.19.

In this case, the formation of the complex can be described by the equation

$$\begin{aligned} &2\textit{trans}\text{-}[Pd(H_2O)_2(NO_3)_2] + 3HAcac \\ &= Pd_2(Acac)_3(NO_3) + 3HNO_3 + 4H_2O. \end{aligned} \qquad (2)$$

An analysis of the solid phases (Table 1, entries 6, 7; Table 2, entries 5, 6) suggests the absence of nitrogen; their formula corresponds to the bischelate complex $Pd(Acac)_2$ (**III**). For $C_{10}H_{14}O_4Pd$ anal. calcd. (%): C, 39.39; H, 4.60; Pd, 34.93.

The yields of the products in all the experiments approximate to 100% (with respect to the proposed formulas), regardless of the synthetic method.

According to the results obtained, the formation of phase **III** in the reaction with crystalline *trans*-[$Pd(H_2O)_2(NO_3)_2$] becomes possible for the higher ratios Pd : HAcac (Table 1, entry 6) compared to the reactions with its aqueous 5 M solution (Table 2, entry 5). For Pd : HAcac = 1 : 1, the reaction gave complex **I**. For Pd : HAcac from 1 : 1.5 to 1 : 3.3 (Table 1) and from 1 : 1.5 to 1 : 2.5 in solution (Table 2), complex **II** was obtained.

Phase **I** is colored bright orange and is insoluble in water or organic solvents. Phase **II** is soluble in ethanol, acetone, and chloroform but is insoluble in water, saturated hydrocarbons, and ether. Product **II** is unstable in ethanol, producing a black precipitate. Phase **III** is soluble in many organic solvents but is insoluble in water.

The complexes were identified by X-ray powder diffraction analysis, vibrational spectroscopy, thermal analysis, and mass spectrometry.

An X-ray powder diffraction experiment was carried out at room temperature on a DRON-3M diffractometer ($R = 192$ mm, CuK radiation, a Ni filter, a scintillation counter, the Bragg–Brentano focusing; $2\theta = 5°–60°$, scan rate 1 deg/min). Samples for the experiment were prepared by grinding in an agate mortar with heptane. The resulting suspension was applied to the polished side of a standard quartz cell and left for evaporation of the solvent. Each prepared sample was a thin even layer 100 μm thick.

IR spectra were recorded on Scimitar FTS-2000 and Vertex 80 FTIR spectrometers in the 80–4000 cm^{-1} range. Samples were prepared as pellets with KBr (400–4000 cm^{-1}) and with polyethylene (80–400 cm^{-1}).

Simultaneous thermal analysis (differential scanning calorimetry + MS analysis of the evolved gas) was performed on a STA409PC Luxx® derivatograph (NETZSCH) connected to a QMS 100 Series gas analyzer. Samples were heated in an Al_2O_3crucible at a rate of 10 K/min in a helium flow (60 ml/min). Experimental data were processed with the Proteus Analysis program package [11].

ESI mass spectra were recorded on an XCT mass spectrometer (Agilent, US). A solution of a test complex in chloroform was syringed into the spectrometer through a stainless needle (Hamilton, US) at a rate of 10 μl/min. Positively charged ions were generated by a potential difference of 500 V between the needle and the walls of the ionization chamber. The solvent was removed by evaporation with nitrogen as a drying gas (200°C, 4 l/min). Then ions traveled through a glass capillary with a potential difference between its ends (from –3500 to 130 V) and a skimmer (40 V) to come into an ion trap. The entrapped ions were analyzed with accumulation for 200 ms.

RESULTS AND DISCUSSION

According to X-ray powder diffraction data, all the products obtained are crystalline solids. Their X-ray diffraction profiles are identical in both the positions and intensities of the reflections, provided that the composition is the same. The profiles of complexes **I** contain much fewer reflections than, and their positions differ from, those in the profiles of complex **II**. The X-ray diffraction profile of phase **III** interpreted from the literature data corresponds in the positions and intensities of the reflections to the known palladium(II) acetylacetonate of the formula $Pd(Acac)_2$ [12]. Phase **II**, which is soluble in organic solvents, was not crystallized into a perfect single crystal suitable for X-ray diffraction analysis because its crystallization gives very thin lamellar needles.

The IR spectra of the phases with the same composition are identical, regardless of the synthetic method. However, it should be noted that this identity is not attained unless the conditions for preparation and homogenization of the reaction mixtures are strictly observed during the synthesis. The vibrational frequencies and their assignments in the spectra of the products obtained in the reaction of crystalline *trans*-$[Pd(H_2O)_2(NO_3)_2]$ with acetylacetone are given in Table 3. The IR spectra of all the complexes show no absorption bands due to the free ligand. The IR spectrum of complex **III** is identical in the positions of the stretches and bends of main functional groups and the chelated hydrocarbon framework of acetylacetone with the literature data for $Pd(Acac)_2$ [12, 13]. In the spectra of complexes **I** and **II**, the positions of the bands due to the skeletal vibrations of the coordinated ligand remain virtually unchanged compared to those for free HL. However, the IR spectrum of complex **II** shows a new band at 1597 cm^{-1} $\nu(C{\cdots}C)$ and $\nu(C{\cdots}O)$, which is absent from the spectrum of complex **I**. Apparently, another type of coordination takes place in complex **II**. This assumption is consistent with chemical and elemental analysis data, which suggest the formation of dimeric product **II**, $Pd_2(Acac)_3(NO_3)$, with one HAcac molecule bridging two Pd atoms. This assumption also agrees with the literature data on bi- and trinuclear palladium(II) complexes with β-diketones as bridging ligands [14]. In [14], it was found that the bridging coordination of β-diketones shifts the ν(CO) and ν(CC) bands to the shorter wavelengths compared to the chelation effect.

The coordination of the nitrate ion in complexes **I** and **II** is evident from the intense absorption bands at 1497 and 1256 cm^{-1} for **I** and at 1492 and 1271 cm^{-1} for **II** (Table 3). In addition, the spectra of both the phases contain intense bands due to the nitrate group at 962 (**I**) and 983 cm^{-1} (**II**), which are forbidden in the spectrum of a free nitrate ion. The absorption wavelengths of the nitrate group in the IR spectra of complexes **I** and **II** are characteristic of bidentate coordination of NO_3^- to metal [15, 16]. The results obtained are not contradictory to the assumption of the bridging coordination of the nitrate group in **I** and **II**. Apparently, complex **I** is a dimer with two nitrate bridges and its formula may be written as $Pd_2(Acac)_2(\mu\text{-}NO_3)_2$. In complex **II**, the palladium atoms are bridged by the nitrate group and an acetylacetone molecule; so its formula is $Pd_2(Acac)_2(\mu\text{-}Acac)(\mu\text{-}NO_3)$.

In the 80–400 cm^{-1} range, the IR spectra of complexes **I–III** contain bands at 360, 334, 302, 290, 265, 248, 216, 133, and 105 cm^{-1} (**I**); 381, 340, 311, 301,

Table 3. Selected vibrational frequencies (cm^{-1}) in the IR spectra of the complexes obtained

$Pd_2(Acac)_2(\mu\text{-}NO_3)_2$	$Pd_2(Acac)_2(\mu\text{-}Acac)(\mu\text{-}NO_3)$	$Pd(Acac)_2$	Assignment
1568	1597 1563	1568	$\nu(CC) + \nu(CO)$
		1548	Composite
1518	1518	1523	$\nu(CO) + \nu(CC)$
1497 sh	1492		$\nu_5(NO_3)$
1412	1424	1420 sh	$\delta(CH) + \nu(CC)$
1385	1380	1386	$\delta_d(CH_3)$
1360	1357	1357	$\delta_s(CH_3)$
1256	1271 s		$\nu_1(NO_3)$
1230	1233	1272 m 1234	$\nu(C\text{–}CH_3) + \nu(CC)$
1195	1198	1197	$\delta(CH) + \nu(C\text{–}CH_3)$
1015	1013	1021	$\rho_r(CH_3)$
962	983		$\nu_2(NO_3)$
	937	936	$\nu(CC)$, $\nu(CO)$
781	787, 811	783	$\pi(CH)$
709 703	698	699	$\nu(C\text{–}CH_3)$, ring bends, $\nu(H\text{–}O_{Acac})$
675	678	677	$\pi(CH_3\text{–}CCO)$
660	664 641	662 643	ring bends + $\nu(M\text{–}O_{Acac})$
	470, 465	465	$\nu(MO) + \nu(C\text{–}CH_3)$
454	448	445	ring bends

279, 265, 228, 219, 139, and 90 cm^{-1} (**II**); 360, 337, 296, 264, 174, and 95 cm^{-1} (**III**).

For $Pd(Acac)_2$, the intense absorption bands at 296 and 264 cm^{-1} were assigned to the $\nu(M\text{–}O_{Acac})$ vibrations [13]. The low-intensity bands at 360 and 337 cm^{-1} are probably due to the skeletal vibrations of HAcac. The bands corresponding to the nitrate groups coordinated in a bidentate fashion ($\nu(M\text{–}O_{NO_3})$) appear at 350–250 cm^{-1} [13] but they are difficult to identify in the spectra of complexes **I** and **II**. To assign them accurately, further investigations are required. The lattice vibrations absorb below 200 cm^{-1}.

The dimeric structure of phase **II** suggested by its IR spectra was confirmed by ESI MS data. A typical ESI mass spectrum of phase **II** is shown in Fig. 1. The most intense peak in the positive-ion spectrum corresponds to $m/z = 511$. The observed isotope distribution is characteristic of a Pd-containing compound. Computer-assisted modeling of the isotope distribution shows that the observed signal is due to an ion with the empirical formula $[C_{15}H_{21}O_6Pd_2]^+$, which corresponds to $[Pd_2(Acac)_3]^+$. Apparently, the nitrate group is eliminated from the complex when its solution is heated in the ionization chamber to 200°C; this agrees with thermal analysis data.

The TGA curve of phase **II** (45.146 mg) with the MS curves of gas evolution in an atmosphere of helium are shown in Fig. 2. The complex is stable below 180°C. About 200°C, the sharp weight loss is accompanied by a strong exothermic effect due to oxidation of the organic part of the complex with the nitrate ion. The main gaseous products of the decomposition are CO, CO_2, and NO, which are manifested in the mass spectrum as molecular ion peaks. The mass spectrum also contains peaks due to the fragmentation ions with $m/z = 15$ (CH_3^+) and 43 (CH_3CO^+) produced by the decomposition of the organic part of the complex. At 220–240°C, trace amounts of acetylacetone are detected. It should be noted that such a decomposition character is typical of complexes combining a sufficiently strong oxidant and organic ligands [17]. The decomposition is virtually completed at 350°C. A slight overestimate of the residual weight (40.77%) versus the theoretical metal content (37.20%) in the initial complex is attributable

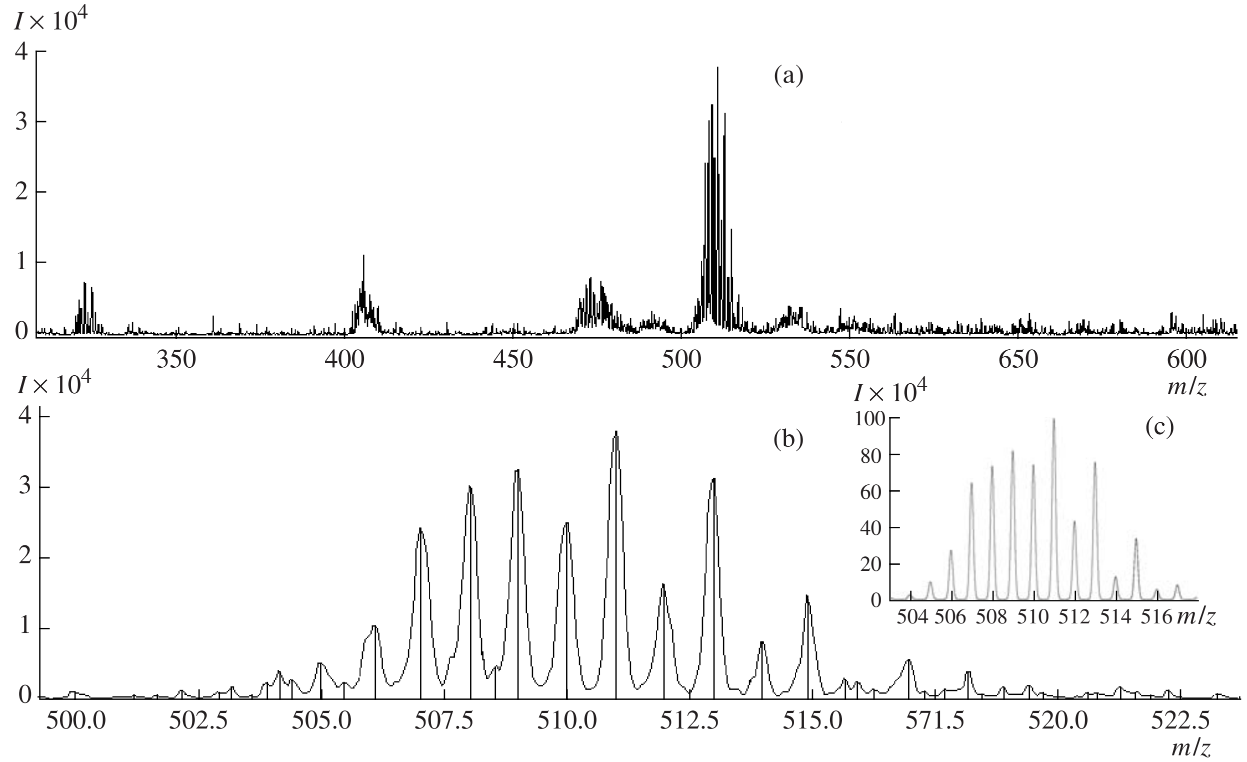

Fig. 1. (a) ESI mass spectrum of complex **II** in $CHCl_3$, (b) isotope clusters at *m/z* = 511, and (c) a computer-assisted model of the isotope distribution in $C_{15}O_6H_{21}Pd_2$.

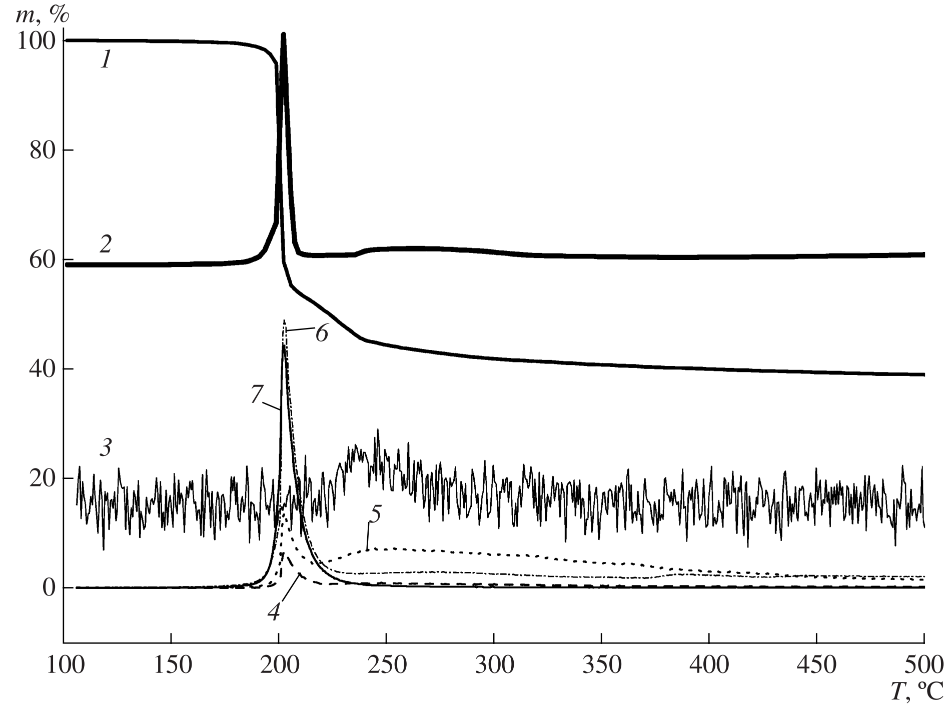

Fig. 2. (*1*) TGA and (*2*) DSC curves of complex **II** in a helium atmosphere (heating rate 10 K/min) and the mass spectra of the evolved gas: (*3*) *m/z* = 100 ($Acac^+$), 1000x magnification; (*4*) *m/z* = 43 (CH_3CO^+); (*5*) *m/z* = 15 (CH_3^+); (*6*) *m/z* = 44 (CO_2^+); (*7*) *m/z* = 30 (NO^+).

to incomplete removal of carbon in a helium atmosphere [17].

Complex **I** decomposes in an inert atmosphere like complex **II**. Complex **I** is stable below 180°C and then a noticeable weight loss takes place. The distinctive feature is that complex **I** decomposes explosively and the mass is ejected from the crucible. Ejection occurred even with a smaller amount of complex **I** (21.630 mg), probably because of a large amount of gases produced by its thermolysis: unlike complex **II**, complex **I** contains two nitrate groups. The mass spectra recorded during the thermolysis of complexes **I** and **II** are fully identical in main decay products.

To sum up, here we were the first to study reactions of crystalline *trans*-$[Pd(H_2O)_2(NO_3)_2]$ with organic ligands (with acetylacetone as an example). We found that a reaction of a Pd(II) salt with HAcac gives the chelate complex $Pd(Acac)_2$ when the molar ratio Pd : HAcac exceeds 1 : 3.6. For Pd : HAcac = 1 : 1 and 1 : (1.5–3.3), the reaction products are the binuclear complexes $Pd_2(Acac)_2(\mu\text{-}NO_3)_2$ and $Pd_2(Acac)_2(\mu\text{-}Acac)(\mu\text{-}NO_3)$, respectively.

A reaction of a freshly prepared, concentrated (5.0 M) aqueous solution of *trans*-$[Pd(H_2O)_2(NO_3)_2]$ occurs in a similar way. The only difference is that the bischelate $Pd(Acac)_2$ can form even at a smaller excess of the ligand (Pd : HAcac = 1 : 3.0).

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