SYNTHESIS AND PROPERTIES
OF INORGANIC COMPOUNDS

Preparative Synthesis of Palladium(II) Acetate: Reactions, Intermediates, and By-Products

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Abstract—Comparison of various laboratory procedures for the synthesis of palladium acetate demonstrated that the purest product containing no nitrite or nitrate impurities is formed in up to 90% yields upon the reaction of palladium nitrate with alkali metal acetates in aqueous acetic acid. Other laboratory syntheses are more labor-consuming and do not ensure high purity of the product. The synthesis by-products are described and possible reaction schemes are proposed.

Palladium acetate $Pd_3(OAc)_6$ (**I**) was first obtained in 1964 by refluxing palladium black in acetic acid containing nitric acid [1, 2]:

$$Pd + AcOH + HNO_3 \longrightarrow Pd_3(OAc)_6 + H_2O + NO + ...$$

The structures of this compound and some its solvates were determined by X-ray diffraction [3, 4]. Palladium acetate has soon found wide use for the preparation of industrial supported catalysts for hydrogenation and oxidative acetoxylation of alkenes. Smaller amounts of this compound are used to prepare other palladium complexes and in homogeneous catalysis.

The same authors reported the preparation of palladium acetate by the reaction of palladium nitrate dihydrate with acetic acid [1, 2] but no details were described:

$$Pd(H_2O)_2(NO_3)_2 + AcOH$$
$$\longrightarrow Pd_3(OAc)_6 + H_2O + HNO_3.$$
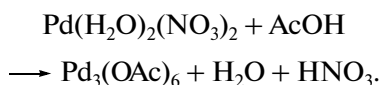
A drawback of both methods is the formation of by-products that are difficult to separate from **I**. Whereas these impurities do not affect the quality of the supported metallic catalysts prepared from palladium acetate, the reagent purity is of prime importance when palladium acetate is used for the synthesis of other compounds, in kinetic measurements and in homogeneous catalysis.

Previously [1, 2], the impurities were removed by long-term refluxing of a palladium acetate solution in acetic acid in the presence of palladium black until evolution of nitrogen oxides NO_x stopped. It was suggested that the impurities represented the palladium nitrate complex $(Pd(NO_2)OAc)$ or even palladium nitrate. A method for the preparation of palladium acetate without nitrogen-containing impurities by dissolving palladium hydroxide $PdO \cdot nH_2O$ in acetic acid was reported [5, 6]. The synthesis of palladium acetate by dissolving palladium metal in acetic acid at 100°C under oxygen pressure in the presence of strong acids is known [7]. A drawback of this method is the formation of an insoluble polymeric by-product. Apart from nitric acid and O_2, nitrogen oxides NO_x and nitrosyl acetate were proposed as oxidants for the synthesis of palladium acetate [8].

It was found [9] that the industrial palladium acetate contains the complex $[Pd_3(OAc)_5(NO_2)]$ (**II**) having a similar structure. This complex is not present in trace amounts: according to our data, the content of **II** in industrial or laboratory-prepared (by a reported procedure [2]) palladium acetate is usually 10–20% and, in some cases, higher. Complex **II** was characterized by IR and ^{1}H NMR spectra; its structure was established by X-ray diffraction analysis. The preparation of **I** free from the impurity of **II** was described [9]. For this purpose, a nitrogen gas stream was passed through a boiling reaction mixture (a suspension of palladium metal in acetic acid with some nitric acid added) to remove dissolved nitrogen oxides. Previously [10], a rather complicated method of purification of palladium acetate was proposed, which included successive treatment with sulfuric acid on heating and with aqueous acetic acid containing sodium carbonate added, but it did not find wide use. Thus, for more than 40 years and until now, instead of pure palladium acetate, mixtures of **I** and **II** have been used in laboratories and in industry all over the word. In the studies concerning homogeneous catalysis and the chemistry of Pd(II) complexes, the difference between the reactivities of **I** and **II** is responsible for unexpected and nonreproducible results. The most vivid example is the series of works [11–13] devoted to successful oxidation reactions of alkanes under mild conditions involving palladium acetate, which could not be reproduced using pure **I** [14, 15].

Recently, the industrial method of the synthesis of palladium acetate was further developed at the Institute of Chemistry and Chemical Technology, Siberian Branch of the RAS (Krasnoyarsk). The reactions that take place between palladium nitrate, acetic acid, ethyl acetate, and nitrogen oxides were studied in detail and various complexes formed in the reaction mixture together with **I** were isolated [16]. In particular, the insoluble polymeric palladium acetate $[Pd(OAc)_2]_n$ (**III**) was characterized in detail for the first time and its structure was determined by powder X-ray diffraction (Rietveld refinement) [17]. Unfortunately, the new method for the preparation of pure palladium acetate by the reaction of palladium nitrate with acetic acid and ethyl acetate proposed in this study [18] proved inapplicable for the use of minor amounts of palladium compounds and reagents in the laboratory. To choose the most reliable laboratory method for the preparation of high-purity compound **I**, we tested a number of previously proposed procedures and made appropriate modifications.

RESULTS AND DISCUSSION

The first procedure that we tested for the preparation of **I** was based on the reaction of palladium nitrate dihydrate with anhydrous acetic acid [16, clause 2.2.3b]. However, instead of the expected crystalline $Pd_3(OAc)_6$, we obtained beige-colored amorphous polymer (**III**) in a 85% yield:

$$Pd(NO_3)_2(H_2O)_2 + AcOH$$
$$\longrightarrow [Pd(OAc)_2]_n + HNO_3 + H_2O.$$
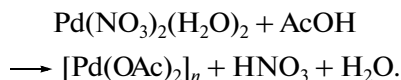
This polymeric complex does not contain even traces of nitrogen-containing compounds.

In independent experiments, we found that in the presence of strong acids (nitric, perchloric, or methanesulfonic acid) in AcOH or diethyl ether, palladium acetate **I** is readily polymerized:

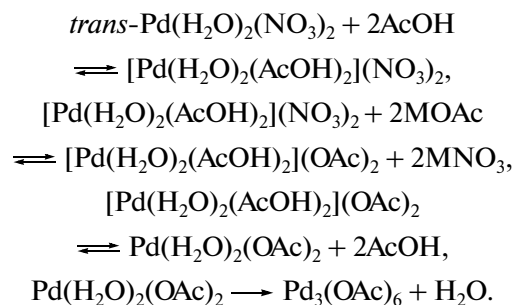$$Pd_3(OAc)_6 + HX + H_2O \longrightarrow [Pd(OAc)_2]_n.$$
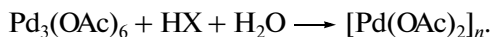
Acetate **I** formed in the reaction of palladium nitrate with acetic acid or its precursor is fast converted to **III** in the presence of nitric acid. In order to reduce the polymer formation in the reaction with palladium nitrate, water was added to acetic acid [16, clause 2.2.3a]. According to our data, the addition of water markedly (to 39%) decreased the yield of polymer **III** and promoted the formation of **I**:

$$Pd(NO_3)_2(H_2O)_2 + AcOH$$
$$\longrightarrow Pd_3(OAc)_6 + [Pd(OAc)_2]_n + HNO_3 + H_2O.$$
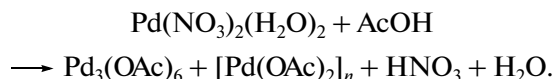
Since the formation of polymeric palladium acetate is catalyzed by strong protic acids, one can expect that the introduction of reagents binding the acid would reduce the yield of **III** and increase the yield of **I**. We were able to completely suppress the formation of **III** and increase the yield of **I** to 90% in the presence of alkali metal acetates.

Presumably, in this case, as in another study [10], the exchange of anionic ligands proceeds, most likely, through the mononuclear palladium aqua complex:

$$trans\text{-}Pd(H_2O)_2(NO_3)_2 + 2AcOH$$
$$\rightleftharpoons [Pd(H_2O)_2(AcOH)_2](NO_3)_2,$$
$$[Pd(H_2O)_2(AcOH)_2](NO_3)_2 + 2MOAc$$
$$\rightleftharpoons [Pd(H_2O)_2(AcOH)_2](OAc)_2 + 2MNO_3,$$
$$[Pd(H_2O)_2(AcOH)_2](OAc)_2$$
$$\rightleftharpoons Pd(H_2O)_2(OAc)_2 + 2AcOH,$$
$$Pd(H_2O)_2(OAc)_2 \longrightarrow Pd_3(OAc)_6 + H_2O.$$

In this case, we did not detect any signs of formation of mixed complex **II**, because the exchange of anionic ligands and dissolution of palladium in a mixture of acetic and nitric acids follow different mechanisms.

The ^1H NMR spectrum showed one singlet signal due to the protons of equivalent OAc groups of complex **I**; no signals of nonequivalent OAc groups of complex **II** were observed.

The reaction of palladium nitrate with acetates in aqueous solutions gives **I** in a low yield (about 30%), apparently, due to hydrolysis.

Palladium acetate obtained by the generally accepted method [2] always contains an impurity of mixed complex **II** apart from **I**. Since the structure and the physical properties of **I** and **II** are similar, these complexes cannot be completely separated by recrystallization. The solubility of **II** in acetic acid considerably exceeds the solubility of **I**; hence, the first crystallized fraction of palladium acetate is the purest, while the following fractions that are evolved as the solution is being concentrated contain **II** in steadily increasing amounts. Recrystallization of crude palladium acetate containing an impurity of **II** from benzene slightly decreases the content of nitrogen in the product. Apparently, the solubilities of complexes **I** and **II** in benzene also do not differ much. In this case, no polymeric acetate **III** was present among the reaction byproducts.

Presumably, the reaction of palladium with a mixture of acetic and nitric acids does not include the intermediate formation of palladium nitrate and involves the solvated nitronium cation or acetyl nitrate. A mixture of nitric acid with acetic anhydride or acetic acid is used in organic chemistry as a mild nitrating agent. The acid quickly reacts with the anhydride to give a mixed anhydride, acetyl nitrate [19]:
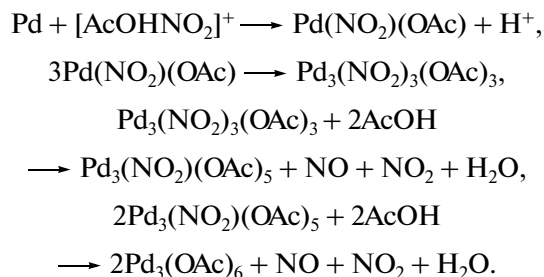
$$HNO_3 + Ac_2O = AcONO_2 + AcOH.$$
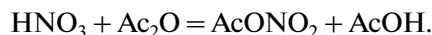
When acetic acid reacts with nitric acid, the protonated acetyl nitrate $[AcOHNO_2]^+$ is formed [20]:

$$AcOH + HNO_3 \rightleftharpoons [AcOHNO_2]^+ + NO_3^- + H_2O.$$

The oxidative addition of this species to Pd(0) (palladium metal) may give the intermediate mononuclear

coordinatively unsaturated Pd(II) nitritoacetate complex, which is transformed to give complexes **II** and **I**:

$$Pd + [AcOHNO_2]^+ \longrightarrow Pd(NO_2)(OAc) + H^+,$$

$$3Pd(NO_2)(OAc) \longrightarrow Pd_3(NO_2)_3(OAc)_3,$$

$$Pd_3(NO_2)_3(OAc)_3 + 2AcOH$$

$$\longrightarrow Pd_3(NO_2)(OAc)_5 + NO + NO_2 + H_2O,$$

$$2Pd_3(NO_2)(OAc)_5 + 2AcOH$$

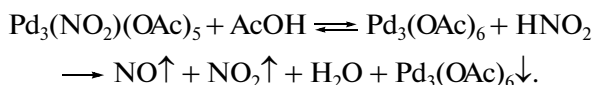$$\longrightarrow 2Pd_3(OAc)_6 + NO + NO_2 + H_2O.$$

This reaction scheme is consistent with the available facts. First, the amount of nitric acid in the reaction mixture (about 1.0 mol per g-at. of palladium [2]) is obviously insufficient for the complete dissolution of the metal to give the nitrate:

$$3Pd + 8HNO_3 = 3Pd(NO_3)_2 + 4H_2O + 3NO,$$

but it is sufficient to completely oxidize Pd(0) to Pd(II) via oxidative addition of acetyl nitrate or its protonated form. These species function in this case as two-electron oxidants. The oxidative addition reactions are widely used for one-step synthesis of various complexes from metals, in particular, platinum metals.

Second, this pattern clearly demonstrates how complex **II** can be formed from palladium metal and acetic and nitric acids. The proper transformation of the nitrate ion to the nitrite ligand is fairly unusual. Third, the successive rather than parallel formation of complexes **II** and **I** is in line with the fact that pure **I** is produced on refluxing a solution of **II** in acetic acid [9, 16, clause 2.2.3d]. It is clear from general considerations that long-term refluxing of a solution of **II** and gas bubbling through the reaction mixture should remove nitrous gases NO_x from the solution and shift the equilibrium toward **I**:

$$Pd_3(NO_2)(OAc)_5 + AcOH \rightleftharpoons Pd_3(OAc)_6 + HNO_2$$

$$\longrightarrow NO\uparrow + NO_2\uparrow + H_2O + Pd_3(OAc)_6\downarrow.$$

Despite the apparent self-consistency of this scheme, we were still unable to obtain pure **I** by bubbling nitrogen or argon as described previously [9]. The results of CHN analysis show that all palladium acetate fractions isolated from the reaction mixture contain approximately equal percentages of nitrogen (as some nitrogen-containing complexes). This was found to be related to the fact that **II** is converted upon thermolysis not only to **I** but also to other palladium compounds and not to the fact that some **II** is retained.

On extraction of crude palladium acetate with benzene, **I** passes to the solution and an insoluble yellow compound with composition close to $Pd_3(CN)(OAc)_5$ or $Pd_4(CN)(OAc)_7$ (**IV**) remains on the filter. The IR spectrum of this compound contains characteristic absorption bands of the acetate and cyanide ligands ($\nu(CN)$, 2212 cm^{-1}; $\nu_{as}(COO)$, 1598 cm^{-1}, $\nu_s(COO) =$ 1420 cm^{-1}).

The formation of $Pd_3(CN)(OAc)_5$ can be described by simple stoichiometric reaction

$$Pd_3(NO_2)(OAc)_5 + CH_3COOH$$

$$= Pd_3(CN)(OAc)_5 + CO_2 + 2H_2O.$$
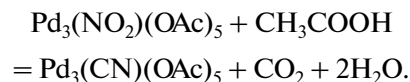
The transformation of the NO_2^- ligand to give the cyanide is described by the equation

$$NO_2^- + CH_3COOH = CN^- + 2H_2O + CO_2.$$
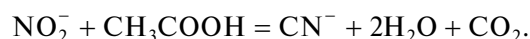
A similar reaction giving cyanides takes place on fusing together alkali metal nitrites and acetates [21]. The formation of insoluble palladium cyanide complexes is responsible for deactivation of the palladium acetate-based catalyst of alkene oxidation in acetic acid containing nitrate ions [22]. In addition, polymeric yellow cyanide acetate complex is formed on refluxing a palladium acetate solution with alkali metal nitrates in acetic acid [23]:

$$Pd_3(OAc)_6 + MNO_3 + AcOH$$

$$\longrightarrow [Pd(CN)OAc]_x + MOAc + CO_2 + NO_2 + ...$$
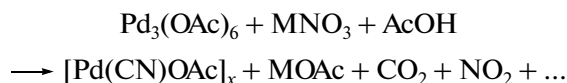
The IR spectrum of this compound exhibit $\nu(CN)$ bands at 2214 cm^{-1} and $\nu(COO)$ bands at 1570 and 1432 cm^{-1}.

Rotary evaporation of the benzene extract after extraction of crude palladium acetate gives pure crystalline acetate **I** containing no nitrogen-containing impurities in an overall yield of about 80%.

Palladium acetate containing no **II** or III impurities can also be obtained by dissolution of palladium oxide hydrate on refluxing in glacial acetic acid as described previously [5, 6]. However, as shown by our experiments, the yield of **I** is relatively low due to competing thermal dehydration of the starting compound to give non-reactive palladium oxide:

$$PdO \cdot nH_2O \rightarrow PdO + nH_2O.$$
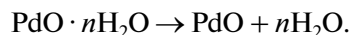
Therefore, among the laboratory methods for the synthesis of pure palladium acetate, the method of choice is the reaction of palladium nitrate dihydrate with alkali metal acetates in aqueous acetic acid at room temperature. The data of chemical analysis indicate that the product purity reaches at least 99.9%.

EXPERIMENTAL

Starting Compounds and Chemicals

We used palladium metal, GOST 14836-82 (99.96%); high-purity grade palladium chloride, TU 6-09-2025-86. Reagent grade glacial acetic acid, GOST 61-75; special-purity grade 18-4 nitric acid, GOST 11185-84; special-purity grade 20-4 hydrochloric acid, GOST 14261-77. Analytical grade potassium hydroxide, GOST 24363-80; sodium borohydride (LABTECH, Russia). Palladium nitrate trans-$[Pd(NO_3)_2(H_2O)_2]$ was synthesized by a known procedure [24]. Palladium black was obtained as described

previously [2]. Reagent grade organic solvents were used as received.

Investigation Methods

The solutions were concentrated in vacuum on a LABOROTA 4000-efficient (Heidolph instruments) rotary evaporator. The elemental analysis of solid compounds (CHN) was carried out on Carlo Erba (Italy) and EA3000 (EuroVector, EC) laboratory CHN(S) analyzers. IR spectra were measured on a Nexus FT IR spectrometer (Nicolet, USA) using an ATR attachment. The photometric determination of the nitrite ion was carried out on a Cary 50 Scan spectrophotometer (Varian). ^{1}H NMR spectra were recorded on a Bruker AVANCE-300 spectrometer.

Attempted Preparation of Palladium Acetate by Described Procedure [16. clause 2.2.3b]

Palladium(II) nitrate (2.500 g) was dissolved in 9 mL of anhydrous acetic acid in a flat-bottomed flask and stirred for 3 h at room temperature. The stirring gradually became impossible due to the formation of a bulky precipitate. The suspension was diluted with acetic acid, and the product was isolated by centrifugation, washed with water and acetone, and dried in vacuum above sodium hydroxide. Instead of crystalline palladium acetate **I**, this gave the polymeric acetate $[Pd(OAc)_2]_n$, yield 1.800 g (85% of theoretical). The obtained compound was a beige-colored amorphous powder insoluble in organic solutions.

For $C_4H_6O_4Pd$ anal. calcd. (%): N, 0.00; C, 21.38; H, 2.67; Pd, 47.40.

Found (%): N, 0.00; C, 22.50; H, 2.33; Pd, 47.35.

IR, cm^{-1}: ν_{as}(COO), 1494; ν_s(COO), 1404; δ(COO) 710.

Synthesis of Palladium Acetate by Described Procedure [16. 2.2.3a]

Palladium nitrate (1.000 g) was dissolved in a mixture of 40 mL of water and 50 mL of acetic acid in a glass beaker with magnetic stirring. After 10 min at room temperature, palladium acetate started precipitating from the solution. After 3 h, yellow-colored crude palladium acetate was filtered off. The compound was washed with glacial acetic acid and ether and dried in vacuum over alkali. The yield was 0.645 g (a mixture of **I** and **III**).

The mixture was extracted with benzene and the resulting solution was filtered (polymeric palladium acetate $[Pd(OAc)_2]_n$ (**III**) remained on the filter). The filtrate was evaporated to dryness at 40°C in a vacuum using a rotary evaporator. The yield of pure acetate **I** was 0.515 g (61%).

Found (%): N, 0.00; C, 20.30; H, 2.64.

IR, cm^{-1}: ν_{as}(COO) 1595, ν_s(COO) 1415, δ(COO) 694.

Modification of Procedure [16. clause 2.2.3a]—the Reaction Performed in the Presence of Alkali Metal Acetates

Palladium nitrate (1.000 g) and sodium acetate NaOAc · 3H$_2$O (1.750 g) were dissolved in a mixture of 40 mL of water and 50 mL of acetic acid, the solution was stirred for 3 h at room temperature, and the crystals of **I** precipitated. After 24 h, the precipitate was filtered off, washed with distilled water, and dried in vacuum. The yield of crude palladium acetate was 0.688 g. The resulting yellow-brown crystals were extracted with benzene, the filtrate was concentrated in vacuum, and the residue was dried in vacuum over alkali. The yield was 0.675 g (80%).

Found (%): N, 0.00; C, 21.42; H, 2.64; Pd, 47.43.

IR, cm^{-1}: ν_{as}(COO) 1596, ν_s(COO) 1414, δ(COO), 694.

^{1}H NM (390 MHz, dry CDCl$_3$, ppm): 215 (s).

The reaction with potassium acetate at the stoichiometric reactant ratio proceeds in a similar way; the yield of **I** reaches 90%. An increase in the MOAc : Pd(H$_2$O)$_2$(NO$_3$)$_2$ molar ratio above 2 : 1 sharply decreases the yield of **I**.

Reaction of Palladium Nitrate with Alkali Metal Acetates in Water

A mixture of palladium nitrate (0.880 g) and sodium acetate (0.900 g) (in 1 : 2 molar ratio) was stirred in a two-phase system consisting of 15 mL of distilled water and 45 mL of chloroform at 20°C for 4 h. Then the reaction mixture was filtered. After breaking of the emulsion, the chloroform layer was separated and concentrated on a rotary evaporator. The residue was dissolved in benzene; evaporation of benzene gave 0.240 g of crystalline palladium acetate (yield 32%). The elemental composition and the IR spectrum of the product correspond to pure **I**.

Generally Accepted Synthesis [2]. Reaction of Palladium Metal with a Mixture of Acetic and Nitric Acids

Palladium black (9.900 g) in 500 mL of acetic and 6 mL of nitric acid was refluxed for 5 h until nitrogen oxide evolution ceased, the hot reaction mixture was filtered and then cooled to room temperature. After 2 h, the separated red-brown crystals were filtered off, washed with acetic acid and ether, and dried in vacuum. The yield was 12.486 g (fraction 1):

Found (%) N, 0.26; C, 21.44; H, 2.38 (up to 12% of **II**).

On concentrating the filtrate, the following fractions of the product were obtained: fraction 2, 2.523 g of a yellow-brown powder.

Found (%): N, 0.4; C, 22.15; H, 2.53 (up to 21% of **II**).

Fraction 3, 0.486 g of a yellow-brown powder.

Found (%): N, 0.70; C, 21.89; H, 1.87 (up to 31% of **II**).

The yield of crude palladium acetate (combined fractions 1–3) containing 12 to 31% of complex **II** was 74%. Further concentration of the reaction mixture gives palladium acetate with even higher contents of nitrogen-containing complexes.

Recrystallization of the crude acetate from benzene slightly decreases the content of the mixed complex **II**.

Modification of Published Method [2] Using Recommendations [9]. Reaction of Palladium Metal with a Mixture of Acetic and Nitric Acids with Argon Bubbling

A suspension of palladium black (4.900 g) in a mixture of 300 mL of acetic acid and 5 mL of nitric acid was refluxed in a flask with intense argon bubbling through the reaction mixture. After 30 min, nitrogen oxide evolution ceased, and after this, heating and bubbling was continued for additional 3 h. After cooling to 20°C, the reaction mixture was concentrated on a rotary evaporator to 150 mL. Filtration of the mixture produced a slight amount of a yellow microcrystalline compound $Pd_4(CN)(NO_2)(OAc)_6$ and the crystalline precipitate of palladium acetate (fraction 1). Concentrating the filtrate produced several more fractions of the product. All of them had roughly the same composition and contained 0.21–0.25% N. The combined fractions were dried in vacuum over NaOH and extracted with benzene, the solvent was removed in vacuum at 40°C. The yield of pure **I** was 7.245 g (70%).

Found (%): N, 0.00; C, 21.30; H, 2.83.

IR: ν(COO), 1596 and 1414 cm^{-1}.

A yellow compound (0.723 g) remained on the filter, its composition was close to $Pd_3(CN)(OAc)_5$ or $Pd_4(CN)(OAc)_7$.

Found (%): N, 1.91; C, 18.82; H, 2.45

IR, cm^{-1}: ν(COO) 1568 and 1432, ν(CN) 2214.

### Reaction of Palladium(II) Hydroxide with Acetic Acid [5, 6]

Palladium chloride (1.900 g) was dissolved with heating in 25 mL of water containing 1.0 mL of concentrated HCl. An aqueous solution of KOH was gradually added with stirring to the resulting solution up to pH 8–9 until brown palladium hydroxide precipitated. The hydroxide was isolated by centrifuging, washed with distilled water, and refluxed in 100 mL of glacial acetic acid for 8 h. The solvent was removed in vacuo and the residue was dried in a vacuum desiccator over alkali. The resulting brown compound with a strong vinegar smell (1.882 g) was extracted with 100 mL of acetone, and the extract was filtered and evaporated to dryness on a rotary evaporator to give 1.550 g of a brown crystalline compound. Black PdO (0.332 g) remained on the filter. Crude palladium acetate was dissolved in 30 mL of methylene dichloride, and the solution was again filtered. The filter with a small amount of PdO was washed with methylene dichloride. Removal of the solvent gave 1.231 g of red-brown crystals of **I** (yield 51%).

The IR spectrum and elemental analysis data of the sample were consistent with the formula $Pd_3(OAc)_6$.

Qualitative Test for Palladium Acetate Purity

The reaction of palladium acetate with CO in acetic acid affords the yellow microcrystalline cluster $Pd_4(\mu\text{-CO})_4(\mu\text{-OAc})_4 \cdot 2AcOH$ (**V**) [25]. However, if the acetate is highly contaminated with **II**, the crimson-colored crystalline complex $Pd_4(\mu\text{-NO})_2(\mu\text{-OAc})_6$ (**VI**) is formed [26] (UV/Vis spectrum in CH_2Cl_2: absorption bands at 35 200 and 15 400 cm^{-1}). During the reaction, the NO_2^- ligands are reduced to coordinated NO:

$$Pd_3(NO_2)(OAc)_5 + CO + AcOH$$
$$\longrightarrow Pd_4(\mu\text{-NO})_2(\mu\text{-OAc})_6 + CO_2 + ...$$
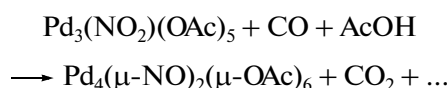
Nitric acid (0.02 mL) was added to palladium acetate (2.500 g) in 100 mL of glacial acetic acid and the solution was stirred in a glass reactor under CO atmosphere for 2 h at 50°C. On cooling of the crimson-colored solution, cluster **V** (if the palladium acetate contained no **II**) or complex **VI** (in the case of high content of **II**) precipitated. Complex **VI** was collected on a filter, washed with benzene, and dried in air. Traces of **V** were removed by dissolution of the complex in chloroform followed by filtering the solution and removal of the solvent from the filtrate in vacuum.

IR spectrum of **VI**, cm^{-1}: ν(NO), 1758 cm^{-1}; ν(COO), 1616, 1572, 1518, 1418, 1377, and 1347 cm^{-1}.

Based on the yield of **VI**, one can estimate the content of **II** in palladium acetate.

Measurement of the Content of NO_2^- Impurity (Complex II) in Palladium Acetate

Vacuum thermolysis of commercial palladium acetate and complex **II** gives N_2O_3 along with methane, CO and CO_2, acetic acid, and acetic anhydride [27]. This reaction can be employed for quantitative determination of the content of **II** in palladium acetate. After transformation of N_2O_3 to the NO_2^- ion via the reaction with alkali, this ion can be determined in an aqueous solution by a known procedure [28]. The content of NO_2^- in **II** was found to be 22.5–23.3%, which is in agreement with the calculated value (6.97% N).

The palladium acetate samples prepared by exchange of palladium nitrate with aqueous acetic acid and alkali metal acetates contain no nitrate and not more than 0.01% of nitrite. The palladium acetate samples obtained by the procedure [2] contain one to several weight percent of nitrite.

ACKNOWLEDGMENTS

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