Characterization of Palladium(II) Azide and Crystal Structure of Bis(azido)bis(pyridine)palladium(II) and Tetramminepalladium Tetraazidopalladate(II)

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Palladium(II) azide (**1**) was synthesized by reaction of palladium nitrate and sodium azide. **1** was characterized by AAS, IR, and ^{14}N-NMR spectroscopy. Bis(azido)bis(pyridine)palladium(II) (**2**) and tetramminepalladium tetraazidopalladate(II) (**3**) were synthesized by a high-yield reaction. Both were characterized by X-ray structural analysis, IR, Raman, and NMR spectroscopy.

Introduction

In the early 1960s Sherif et al. examined the first palladium azide complexes in solution photometrically. The existence of $[Pd(N_3)_2Cl_2]^{2-}$, $[Pd(N_3)_4]^{2-}$, and $Pd(N_3)^+$ was postulated in accordance with absorption measurements.[1] Palladium(II) azide was first synthesized by Clem et al.[2] Spectroscopic studies failed because the compound exploded. In this work palladium(II) azide has been characterized by AAS, IR, and ^{14}N-NMR spectroscopy. Beck et al. synthesized some interesting palladium azide compounds in the late 1960s.[3–5] Tetraphenylarsonium tetraazidopalladate(II) has been synthesized as shown in Equation 1. In this study the structure of the tetraazidopalladate(II) anion has been determinated by X-ray structure investigation.

$$Pd(NO_3)_2 \;+\; 4\,NaN_3 \;+\; 2\,As(C_6H_5)_4Cl \xrightarrow[\substack{-\,2\,NaNO_3 \\ -\,2\,NaCl}]{H_2O} [As(C_6H_5)_4]_2[Pd(N_3)_4] \qquad (1)$$

Results and Discussion

Synthesis of 1

Palladium(II) azide (**1**) can be synthesized by reaction of two equivalents of sodium azide with palladium nitrate in water (Equation 2). A black-brown compound precipitates which is highly explosive if dried in air. Attempts to dry the product in the desiccator failed because of the explosivity of **1**. The compound detonates at 117°C. The palladium determination with AAS spectroscopy shows a result of 46.55% of palladium. For coordinated water the calculated palladium percentage is 46.98%, so it can be expected that there is water coordinated. The IR spectrum of the explosion gases shows a weak absorption at 3650 cm^{-1} for OH streching vibrations. An IR spectrum has been measured on a KBr plate. It was not possible to measure in Nujol because of the explosivity of the compound. The IR spectrum shows five absorptions at 3450 cm^{-1} for OH streching vibrations, at 2067 cm^{-1} for the antisymmetric stretching vibration of the azide group, 1205 cm^{-1} for the symmetric stretching vibration of the azide group, 559 cm^{-1} for the deformation vibration of the azide group and at 438 cm^{-1} for the palladium−nitrogen stretching vibration. The strong intensity of the symmetric stretching vibration which is not allowed for the azide ion, points to a covalent palladium−azide bond.[3] The fact that there is only one signal for the antisymmetric streching vibration of the azide group concludes that the palladium atom is surrounded by chemically equivalent azide groups as shown in Figure 1.

$$Pd(NO_3)_2 \;+\; 2\,NaN_3 \xrightarrow[-\,2\,NaNO_3]{H_2O} Pd(N_3)_2 \qquad (2)$$

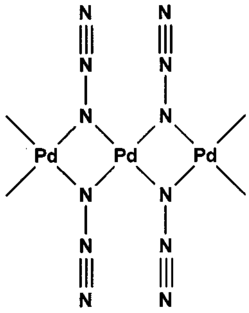

Figure 1. Structure model of **1**

Compound **1** crystallizes probably in chains in which the palladium atom is surrounded in a square-planar fashion by bridging azide groups. The ^{14}N-NMR spectrum of **1** shows the expected signals for covalently bonded azides. The N2 atom shows a resonance at $\delta = -129$, the N3 atom at $\delta = -226$, and the N1 atom a very weak resonance at $\delta = -328$. The solution of **1** in pyridine shows the same

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resonances as for **2** in the ^{14}N-NMR spectrum. Probably pyridine coordinates at the palladium center to form **2**.

Synthesis of 2

Palladium nitrate reacted with an excess of pyridine and sodium azide to form orange-yellow prisms of bis(azido)-bis(pyridine)palladium(II) (Equation 3). The compound is not explosive. At a temperature of 165 °C the compound decomposes.

$$Pd(NO_3)_2 \quad + \quad 2\,py \quad + \quad 2\,NaN_3 \quad \xrightarrow[-\,2\,NaNO_3]{H_2O} \quad Pd(py)_2(N_3)_2 \qquad (3)$$

Crystal Structure of 2

Crystals of **2** (Figure 2) are monoclinic, space group *C*2/*c* with 4 molecules in the unit cell. The palladium atom is surrounded by four nitrogen atoms, two of the azide group and two of the pyridine rings. All eight nitrogen atoms lie in plane. The pyridine rings are out of this plane. The distance between two palladium atoms is 3.86 Å. The crystals form chains in which all molecules are congruent. The plane of the nitrogen atoms of the next chain is twisted 90° to the nitrogen plane of the other chain. Bond lengths and bond angles are compiled in Table 1.

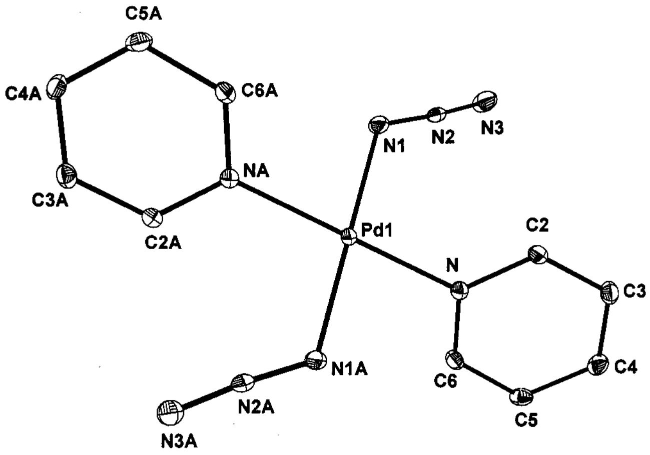

Figure 2. Molecular structure of **2** (the thermal ellipsoids represent a 25% probability)

Table 1. Selected bond lengths [Å] and angles [°] for **2**

Pd(1)−N(1)	2.037(2)	N(1)−N(2)	1.203(2)
Pd(1)−N(A)	2.0417(18)	N(2)−N(3)	1.150(3)
Pd(1)−N(1A)	2.037(2)	C(2)−C(3)	1.387(4)
Pd(1)−N	2.0417(18)	C(3)−C(4)	1.378(4)
N−C(6)	1.334(3)	C(4)−C(5)	1.384(4)
N−C(2)	1.356(4)	C(5)−C(6)	1.388(3)
N(1)−Pd(1)−N(1A)	180	N(1)−Pd(1)−N(A)	85.78(8)
N(1A)−Pd(1)−N(A)	94.21(8)	N(1)−Pd(1)−N	94.21(8)
N(1A)−Pd(1)−N	85.79(8)	N(A)−Pd(1)−N	180
C(6)−N−C(2)	118.6(2)	C(6)−N−Pd(1)	120.0(2)
C(2)−N−Pd(1)	121.3(2)	N(2)−N(1)−Pd(1)	125.5(2)
N(3)−N(2)−N(1)	175.2(2)	N−C(2)−C(3)	121.6(3)
C(4)−C(3)−C(2)	119.5(3)	C(5)−C(4)−C(3)	118.8(2)
C(4)−C(5)−C(6)	119.0(2)	N−C(6)−C(5)	122.5(2)

The N1−N2 bond length is 1.203(2) Å; thus, the bond order is between one and two. The covalent radius[6] for a single-bonded nitrogen atom is r_{cov} = 0.7 Å, 0.6 Å for a double-bonded nitrogen atom, and 0.55 Å for a triple-bonded nitrogen atom. The bond order for the N2−N3 [1.150(3) Å] is between two and three. The angle of the azide group (N1−N2−N3) is 175.2(2)°, the angle between the palladium atom and the azide group (Pd1−N1−N2) is 125.5(2)°.

Synthesis of 3

Compound **3** was synthesized by reaction of $Pd(NH_3)_4Cl_2$ with sodium azide in water (Equation 4). The compound can be handled, but it detonates by shock or by friction. It has been fully characterized by IR, Raman, and ^{14}N-NMR spectroscopy. An X-ray structure determination was also performed for this compound.

$$2\,Pd(NH_3)_4Cl_2 \quad + \quad 4\,NaN_3 \quad \xrightarrow[\substack{-\,4\,NaCl \\ -\,4\,NH_3}]{H_2O} \quad [Pd(NH_3)_4][Pd(N_3)_4] \qquad (4)$$

The ^{14}N-NMR spectrum shows the expected signals for covalently bonded azides.[7−9] But two signals can be seen for the N3 nitrogen atom at $\delta = -231$ and -234. The crystal structure determination shows only equivalent N3 nitrogen atoms, so that only one signal for the N3 atom is expected. Consequently, there are no equivalent N3 nitrogen atoms in solution. There may be a coordination between half of the N3 nitrogen atoms and the electrophilic center of the tetramminepalladium cation. This coordination would lead to different N3 nitrogen atoms.

Crystal Structure of 3

Compound **3** crystallizes in the othorhombic space group *I*4/*m* with two molecules in the unit cell (Figure 3). The crystallographic data and refinement details for compound **3** are summarized in the Experimental Section. The bond lengths and bond angles are compiled in Table 2.

Compound **3** displays a salt-like structure with a Pd−Pd interaction between cation and anion. The Pd−Pd distance is 3.0420 Å. The dihedral angle between the ammine and the azide ligands is 45°. The cation and anion are both ideal square-planar. The N1−N2 distance of the azide group is 1.211(4) Å. This corresponds with a bond order between one and two. The N2−N3 distance is 1.143(4) Å. The bond order of this bond lies between two and three. The azide group is nearly linear with an N1−N2−N3 angle of 178.3(3)°. The angle between the palladium atom and the N2 atom of the azide group is 116.8(2)°. Therefore the structure of the anion looks like a "wind wheel" (Figure 4). The bond lengths and angles are similar to the valence-isoelectronic $[Au(N_3)_4]^-$ anion which shows the same wind-wheel-like structure. This compound crystallizes even with

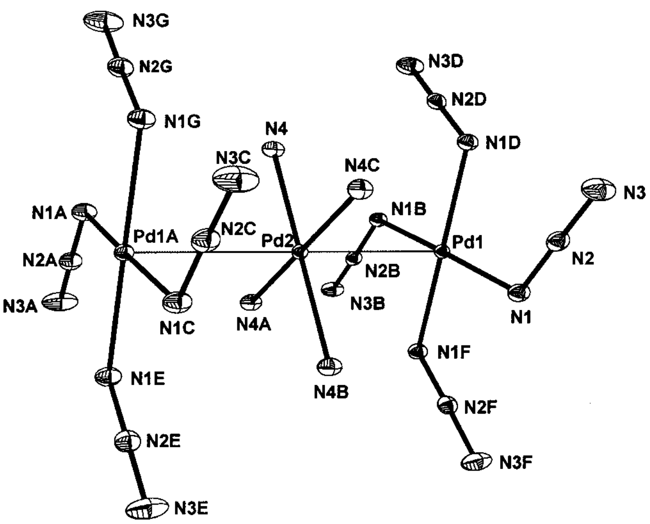

Figure 3. Molecular structure of **3** (the thermal ellipsoids represent a 25% probability)

Table 2. Selected bond lengths [Å] and angles [°] for **3**

Pd(1)−N(1)	2.056(2)	Pd(2)−N(4)	2.039(3)
Pd(1)−Pd(2)	3.0420(2)	N(1)−N(2)	1.211(4)
N(1A)−Pd(1)−N(1)	90	N(2)−N(3)	1.143(4)
N(2)−N(1)−Pd(1)	116.8(2)	N(3)−N(2)−N(1)	178.3(3)

the same coordination number like **3** and not as reported with $Z = 1$.[10]

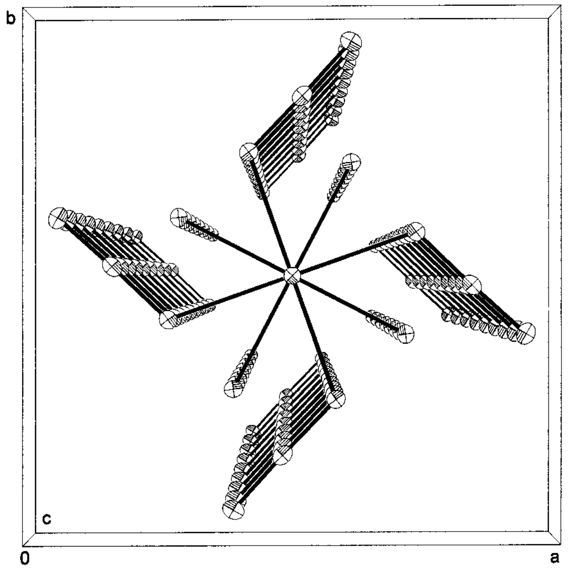

Figure 4. Perspective view of **3** along the *c* axis (the thermal ellipsoids represent a 25% probability)

Experimental Section

General Remarks: ***CAUTION:*** Palladium azide compounds are explosive! **1** is highly explosive. It detonates immediately by touching. Only PE equipment should be used during the preperation and handling of palladium azides. Safety equipment like leather gloves and face-shield is recommended.

NMR: Jeol EX400 Delta [^{1}H, ^{13}C, chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shifts of residual solvent signals; ^{14}N, external standard: $\delta(CH_3NO_2) = 0.00$]. − IR: Nicolet 520 FT-IR (as KBr pellets or on a KBr plate). − Raman: Perkin Elmer Spectrum 2000R NIR FT. − CHN analyses: Analysator Elementar Vario EL. − AAS: Spectrometer 1100B. − MS: Finnigan MAT 90. − Compound **1** was prepared according to the procedure given in the literature.[3]

Palladium(II) Azide (1): A solution of 0.078 g ($1.2 \cdot 10^{-3}$ mol) of NaN_3 in 3 mL of water was added slowly under stirring at room temperature to a solution of 0.138 g ($0.6 \cdot 10^{-3}$ mol) of $Pd(NO_3)_2$ in 10 mL of water. A black-brown compound precipitated. The compound was filtered off after 5 h of stirring and washed with water. The compound was dried in air. Yield: 90.0 mg (80%), black-brown compound; m.p. 117°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3450 (OH) (vw), 2388 [$2 \times \nu_s(N_3)$] (m), 2067 [$\nu_{as}(N_3)$] (s), 1617 (w), 1400 (vw), 1205 [$\nu_s(N_3)$] (s), 734 (w), 551 [$\delta(N_3)$] (w), 438 (PdN) (s). − ^{14}N NMR (pyridine, 29 MHz, 25°C): $\delta = -64$ (s, $N_{pyridine}$), −129 (s, N2), −226 (s, N3), −328 (s, N1). − PdN_6 (190.46): calcd. Pd 55.88; $PdN_6 \cdot 2\ H_2O$ (226.49): calcd. Pd 46.98; found Pd 46.53.

Bis(azido)bis(pyridine)palladium(II) (2): 5 mL ($6.18 \cdot 10^{-2}$ mol) of pyridine and a solution of 0.078 g ($1.2 \cdot 10^{-2}$ mol) of NaN_3 in 3 mL of water were added slowly under stirring at room temperature to a solution of 0.138 g ($0.6 \cdot 10^{-3}$ mol) of $Pd(NO_3)_2$ in 15 mL of water. An orange compound precipitated. Compound **2** was filtered off after 5 h of stirring and washed with water. The compound was recrystallized from hot pyridine and dried in vacuo. Yield: 196.0 mg (94%), orange crystals; m.p. 165°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3094 (CH) (w), 2030 [$\nu_{as}(N_3)$] (s), 1606 (CC) (s), 1451 (s), 1291 [$\nu_s(N_3)$] (s), 1153 (m), 766 (m), 693 (s), 581 [$\delta(N_3)$] (w), 460 (PdN) (s). − Raman (400 scans, 40 mW, 180°, 20°C): $\tilde{\nu}$ = 3084 (CH) (3), 2044 [$\nu_{as}(N_3)$] (1.5), 1570 (1.5), 1294 [$\nu_s(N_3)$] (2), 1152 (1.5), 1024 (8), 372 (7.5), 215 (7), 121 (10). − ^{1}H NMR ([D$_6$]acetone, 400 MHz, 25°C): δ = 8.77 (d, NC*H*), 8.10 (m, NCHCHC*H*), 7.67 (m, NCHC*H*). − ^{13}C NMR ([D$_6$]acetone, 101 MHz, 25°C): δ = 152.5 (s, N*C*H), 140.5 (s, NCHCH*C*H), 127.0 (s, NCH*C*H). − ^{14}N NMR ([D$_6$]acetone, 29 MHz, 25°C): $\delta = -129$ (s, N2), −158 (s, $N_{pyridine}$), −225 (s, N3), −328 (s, N1). − MS (EI, 70 eV); *m/z* (%): 79 (100) [$C_5H_5N^+$], 52 (50). − $C_{10}H_{10}N_8Pd$ (348.66): calcd. C 34.45, H 2.89, N 32.14; found C 33.92, H 2.89, N 31.85.

Crystal Structure Analysis of 2: $C_{10}H_{10}N_8Pd$, $M = 348.66$, crystal size: 0.3 × 0.2 × 0.2 mm, orange-yellow prism, monoclinic, space group *C*2/*c*, $a = 16.1667(2)$, $b = 3.855(2)$, $c = 20.3238(2)$ Å, $\beta = 101.494(1)$, $V = 1241.26(2)$ Å^3, $Z = 4$, $d_{calcd.} = 1.866$ Mg/m^3, $\mu = 1.495$ mm^{-1}, $F(000) = 688$. Siemens CCD Area detector, scan type: hemisphere, Mo-K_α, $\lambda = 0.71073$ Å, $T = 193$ K, 2θ range = 4.10−58.04° in $-18 \leq h \leq 18$, $-4 \leq k \leq 4$, $-26 \leq l \leq 25$, reflections collected: 1650, independent reflections: 1019 ($R_{int} = 0.0132$), observed reflections: 943 [$F > 4\sigma(F)$]. Structure solution and refinement program: SHELXS-97 (G. M. Sheldrick, University of Göttingen, Germany, **1997**), direct methods, data-to-parameter ratio: 9.3:1 {8.7:1 [$F > 4\sigma(F)$]}, final *R* indices [$F > 4\sigma(F)$]: $R1 = 0.0204$, $wR2 = 0.0557$, $R1 = 0.0220$, $wR2 = 0.0564$ (all data), GOF on $F^2 = 1.080$, largest and mean Δ/σ: 0.001, 0.000, largest difference peak/hole: 0.449, −0.566 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-107249. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Tetramminepalladium Tetraazidopalladate(II) (3): A solution of 0.078 g ($1.2 \cdot 10^{-3}$ mol) of NaN_3 in 5 mL of water was added slowly under stirring at room temperature to a solution of 0.147 g ($0.6 \cdot 10^{-3}$ mol) of $Pd(NH_3)_4Cl_2$ in 30 mL of water. The solution was concentrated in air. Orange-brown needles precipitated. Compound **3** was filtered off and washed with water. The compound was dried in vacuo. Yield: 127.0 mg (94%), orange-brown needles; m.p. 146°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3293 (NH) (br.), 3146 (NH) (sh), 2017 [$\nu_{as}(N_3)$] (s), 1622 (w), 1287 [$\nu_s(N_3)$] (vs), 1248 [$\nu_s(N_3)$] (sh), 755 (s), 587 [$\delta(N_3)$] (w), 398 (PdN) (s). − Raman (810 scans, 30 mW, 180°, 20°C): $\tilde{\nu}$ = 3124 (NH) (1.5), 2054 [$\nu_{as}(N_3)$] (3.5), 1274 [$\nu_s(N_3)$] (2), 1056 (2), 495 (3.5), 386 (PdN) (10), 185 (7), 146 (7). − ^{14}N NMR ([D$_6$]acetone, 29 MHz, 25°C): $\delta = -129$ (s, N2), -231 (s, N3), -234 (s, N3), -338 (s, N1), -414 (s, *N*H$_3$). − MS (EI, 70 eV); *m*/*z* (%): 212 (25) [Pd_2^+], 69 (83), 55 (100), 45 (57). − $H_{12}N_{16}Pd_2$ (449.06): calcd. H 2.69, N 49.91; found H 2.45, N 49.00.

Crystal Structure Analysis of 3: $H_{12}N_{16}Pd_2$, $M = 449.06$, crystal size: 0.20 × 0.12 × 0.10 mm, orange-brown needle, orthorhombic, space group *I*4/*m*, $a = 9.8789(2)$, $b = 9.8789(2)$, $c = 6.0840(2)$ Å, $V = 593.75(3)$ Å^3, $Z = 2$, $d_{\text{calcd.}} = 2.512$ Mg/m^3, $\mu = 3.045$ mm^{-1}, $F(000) = 432$. Siemens CCD Area detector, scan type: hemisphere, Mo-K_α, $\lambda = 0.71073$ Å, $T = 183$ K, 2θ range = 5.84−54.86° in $-12 \le h \le 12$, $-12 \le k \le 12$, $-6 \le l \le 5$, reflections collected: 1650, independent reflections: 327 ($R_{\text{int}} = 0.0144$), observed reflections: 282 [$F > 4\sigma(F)$]. Structure solution and refinement program: SHELXS-97 (G. M. Sheldrick, University of Göttingen, Germany, **1997**), direct methods, data-to-parameter ratio: 9.1:1 {7.8:1 [$F > 4\sigma(F)$]}, final R indices [$F > 4\sigma(F)$]: $R1 = 0.0134$, $wR2 = 0.0369$, $R1 = 0.0161$, $wR2 = 0.0376$ (all data), GOF on $F^2 = 1.172$, largest and mean Δ/σ: 0.000, 0.000, largest difference peak/hole: 0.315, -0.583 e Å^{-3}. Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-410384.

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