

Palladium Chemistry in Anhydrous HF/AsF₅ Superacid Medium

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Pd metal dissolves in anhydrous HF (aHF) acidified with AsF₅ in the presence of F₂ at ≈298 K to give a blue-green solution from which green Pd(AsF₆)₂ can be isolated. The latter was also prepared by the interaction of PdF₂ and AsF₅ in aHF or by the reaction between PdO and F₂ in aHF acidified with AsF₅. Powdered Pd(AsF₆)₂ slowly loses AsF₅ in a dynamic vacuum. It can therefore be isolated from solution at $T < 253$ K. Single-crystals of Pd(AsF₆)₂ were prepared by solvothermal synthesis from a Pd/AsF₅/F₂/aHF mixture at 393 K. Pd(AsF₆)₂ is triclinic with $a = 500.9(5)$, $b = 538.3(5)$, $c = 864.9(9)$ pm, $\alpha = 74.46(3)$, $\beta = 89.97(4)$, $\gamma = 62.47(2)^\circ$, $V = 0.1972(3)$ nm³, and $Z = 1$, space group $P\bar{1}$ (No. 2). The six-coordinate Pd atoms (coordinated with fluorine) are well sep-

arated by isolated AsF₆ units. In the 2–175 K temperature range Pd(AsF₆)₂ follows the Curie–Weiss law with $\mu_{\text{eff}} = 3.53$ B.M., $T_n = 8$ K and $\theta_p = -13$ K. Because of cation-anion interactions, the AsF₆[−] anions deviate from ideal O_h symmetry. The reduced symmetry can be seen in vibrational spectra, where splitting of the anion vibrational modes can be observed. The oxidation of Pd metal or PdO with F₂ in neutral aHF yielded Pd₂F₆. No reaction was observed between Pd, PdO or Pd₂F₆ and AsF₅ in aHF. All attempts to prepare PdFAsF₆ were unsuccessful.

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Introduction

Usually, self-ionization of pure anhydrous hydrogen fluoride (aHF) yields solvated protons H⁺_(solv) (the acid) and solvated fluoride anions F[−]_(solv) (the base).^[1] On addition of Lewis bases (fluoro bases) or acids (fluoro acids) to aHF, a massive displacement in aHF self-ionization occurs. In this way it is possible to adjust the acidity (or basicity) of aHF. Addition of Lewis bases (donors of F[−], e.g. CsF) causes an enhancement of the F[−] concentration, that is, an increase in basicity (a decrease in acidity) and, conversely, addition of Lewis acids (acceptors of F[−], e.g. AsF₅) causes a lowering of the F[−] concentration and consequently an increase in acidity (decrease in basicity) of aHF. In absolutely pure aHF, the concentration of F[−]_(solv) equals that of H⁺_(solv) and aHF is neutral. We can talk about acidic, neutral and basic aHF, expressions which are generally accepted in fluorine chemistry and are also generally valid for any other solvent (including water) which can be acidic, neutral or basic.^[1] The acidity (or basicity) of the solvent is

important for the generation of desired oxidation states of transition metals.^[1–6] The oxidation of noble metals by elemental fluorine conveniently shows the influence of acidity of aHF on the final oxidation state of the noble metal in the products. Basic aHF, with a high concentration of F[−]_(solv), favours anion formation with the metal in a high oxidation state, whereas acidic aHF, with a low concentration of F[−]_(solv), favours compounds with the metal in a cationic form and a low oxidation state.^[7,8] In neutral aHF, binary fluorides are formed.

In previous investigations it was found that oxidation of palladium metal by elemental fluorine in basic aHF yielded the Pd(IV) high oxidation state in the PdF₆^{2−} anion (Li₂PdF₆^[8], K₂PdF₆^[8] (NH₄)₂PdF₆^[7]), whereas in acidic aHF (acidified with SbF₅) the final product of oxidation, i.e. Pd(SbF₆)₂^[8] contained a low-oxidation state Pd^{II} cation. Our preliminary results showed that clear blue-green solutions of the Pd^{II} salt [Pd(AsF₆)₂], when treated with alkali fluoride in aHF, gave a light-brown precipitate of a new variety of PdF₂ (low-temperature form),^[9] while the same procedure on Pd(SbF₆)₂ gave the previously known lilac rutile-type form of PdF₂.^[8] For that reason we decided to study palladium chemistry in AsF₅/aHF superacid media in more detail. The aim of this work was to find out what happens when palladium metal and different palladium compounds (i.e. PdO, PdF₂ and Pd₂F₆) are treated with aHF acidified with AsF₅ (a Lewis acid weaker than SbF₅) in the presence or absence of elemental fluorine. The results of investigations of palladium chemistry in neutral aHF are also reported.

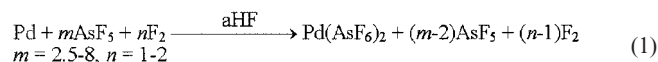
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Results and Discussion

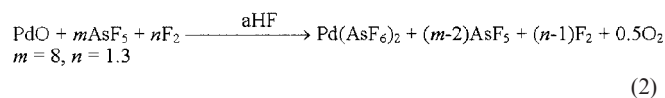
Syntheses

AsF₅ is able to oxidize 3*d*-metals at room temperature using AsF₃ or anhydrous hydrogen fluoride (aHF) as the solvent, giving *M*(AsF₆)₂, *M*FAsF₆ or *M*(AsF₆)₂·2AsF₃ types of compounds.^[10] In contrast, the use of elemental fluorine is necessary for the oxidation of 4*d*- and 5*d*-metals,^[7,8] including palladium, in aHF acidified with AsF₅. In the superacidic system AsF₅/aHF, palladium was slowly oxidized and finally completely dissolved yielding a green-blue solution of solvated Pd²⁺ cations, from which green Pd(AsF₆)₂ was isolated [Equation (1)]

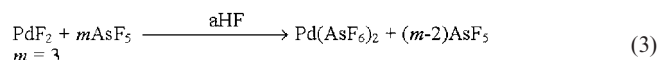


There was no noticeable difference in the course of the reactions when different forms of Pd metal were used (Pd black, gray or sponge). In some experiments with Pd and AsF₅ in aHF we observed a green-blue solution, indicating a possible reaction. Later we discovered, however, that the reason lay in impure AsF₅ contaminated by traces of fluorine. When superacid AsF₅/aHF was first treated with hydrogen and then allowed to react with palladium, no such coloring of the liquid phase was observed.

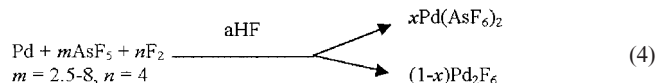
PdO does not dissolve in an AsF₅/aHF superacidic system, contrary to some other oxides of 3*d*- and 5*f*-transition metals which can yield oxonium salts.^[11,12] On addition of elemental fluorine to a suspension of PdO in AsF₅/aHF, the reaction proceeds with formation of a green-blue solution from which Pd(AsF₆)₂ can be isolated [Equation (2)].



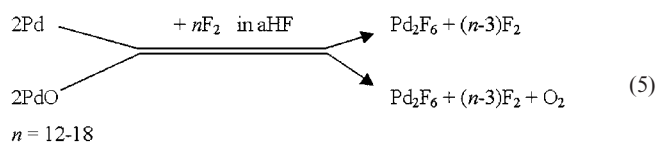
Pd(AsF₆)₂ can be prepared directly by the reaction between PdF₂ and AsF₅ in aHF [Equation (3)].



For the first two reactions [Equations (1) and (2)] the amount of fluorine is very important. In the literature it has been reported that addition of fluorine to a solution of AgF₂ in AsF₅/aHF causes the partial oxidation of Ag^{II} to Ag^{III} and formation of (Ag^{II}F)₂(Ag^{III}F₄)AsF₆.^[13] On prolonged exposure to F₂ of the highly aHF-soluble Au(SbF₆)₂, part of the Au^{II} is oxidized to Au^{III}, yielding mixed-valence, poorly soluble Au^{II}(SbF₆)₂Au^{III}(Au^{III}F₄)₂.^[5] If the excess of fluorine in reactions (1) and (2) is too great, black aHF-insoluble mixed-oxidation state Pd₂F₆, i.e. Pd^{II}(Pd^{IV}F₆)₂,^[14] is formed besides aHF-soluble Pd(AsF₆)₂ [Equation (4)].



The precipitation of black Pd₂F₆ also occurred when fluorine was added to a clear green-blue solution of solvated Pd²⁺ in AsF₅/aHF. Reactions between Pd or PdO and F₂ in neutral aHF also yielded Pd₂F₆ [Equation (5)].

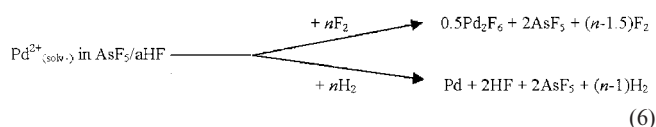


Even when PdO and F₂ in aHF were left to react for a longer time (48 days) than Pd and F₂ in aHF (4 days), unchanged PdO was still present in the solid and only ≈60 mol % of starting PdO was converted into Pd₂F₆. It is also worth noting that there was no sign of any reaction between PdF₂ and F₂ in aHF, even after several days, probably due to kinetic reasons.

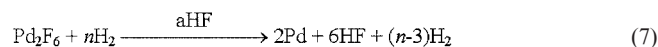
The formation of Pd₂F₆ shows that the oxidation of Pd metal by fluorine can also partly proceed to Pd(IV) in acidic aHF [Equation (4)] as well as in basic^[7,8] and neutral aHF media [Equation (5)].

This is in agreement with previous results showing that, by using a stronger oxidizer (KrF₂) than fluorine in neutral or acid aHF (acidified with AsF₅), all Pd is oxidized to Pd^{IV}F₄.^[15] The main driving forces for the formation of Pd(AsF₆)₂ or PdPdF₆ are the fluoride ion affinities of AsF₅ (PdF₄) and the lattice energy differences between PdF₂ and the complex fluoroanion salts Pd(AsF₆)₂ (PdPdF₆). Since even PdF₄ prepared in situ does not react with AsF₅^[15] and precipitates on addition of AsF₅ to aHF solutions of PdF₆²⁻ alkali metal salts,^[16] it can be concluded that the Lewis acidity (fluoroacidity or fluoride ion affinity) of PdF₄ is weaker than that of AsF₅. The driving force for the formation of Pd₂F₆ (PdF₂ + PdF₄), despite the presence of the stronger fluoro acid AsF₅, is its high lattice energy. This explains why AsF₅ is not able to precipitate PdF₄ from Pd₂F₆ although it has a higher fluoride ion affinity than PdF₄.

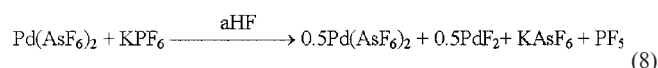
Solvated Pd^{II} in green-blue solutions of Pd(AsF₆)₂ can, on the other hand, be easily oxidized or reduced, yielding finely powdered Pd₂F₆ or Pd metal, respectively [Equation (6)].



Additionally it was found that Pd₂F₆ can also be reduced by hydrogen in aHF yielding powdered Pd metal [Equation (7)].



To prepare pure Pd(AsF₆)₂ according to reactions (1), (2) and (3), the temperature of recovery from solution is important. It was found that Pd(AsF₆)₂ releases AsF₅ in a dynamic vacuum. Pure Pd(AsF₆)₂ can be isolated from solution in aHF by pumping away volatiles at temperatures lower than 253 K. At room temperature, the isolated products had varied compositions “PdF_x(AsF₆)_{2-x}” with 0 < x ≤ 1 depending on temperature, time of isolation and vacuum conditions. For all compositions, the X-ray powder diffraction patterns showed only lines which could be attributed to Pd(AsF₆)₂. Even the X-ray powder pattern of the phase close to a “PdFAsF₆” composition was the same as that of Pd(AsF₆)₂. We also tried to prepare PdFAsF₆ by displacing a weak acid from its alkali metal salt, similar to that reported for AgFBiF₆ from Ag(BiF₆)₂ [17] but, instead of PdFAsF₆, a mixture of Pd(AsF₆)₂ and a low-temperature modification of PdF₂ [9] was always obtained [Equation (8)].



On the basis of these results we conclude that phases with compositions PdF_x(AsF₆)_{2-x} (0 < x ≤ 1) are mixtures of Pd(AsF₆)₂ and PdF₂ and not mixtures of Pd(AsF₆)₂ and PdFAsF₆. The possible preparation and existence of PdFAsF₆ is thus still in question. The instability of Pd(AsF₆)₂ in a dynamic vacuum could be a consequence of the inadequate fluoroacidity of AsF₅. When a stronger fluoroacid SbF₅ (FIA[SbF₅,g] ≈ −506 (± 63) kJ/mol)^[18] was used instead of AsF₅ (FIA[AsF₅,g] ≈ −421 (± 22) kJ/mol)^[18] the resultant Pd(SbF₆)₂ was stable at room temperature.^[8] However care must be exercised in this type of comparison, in that the relative volatilities of AsF₅ and SbF₅ are also important factors in the stabilities of the resultant Pd(AsF₆)₂ and Pd(SbF₆)₂.

Crystal Structure of Pd(AsF₆)₂

Pd(AsF₆)₂ crystallizes in the same structural category as many other compounds obtained in the systems MF₂/XF₅ (M = transition metal, XF₅ = Lewis acid), e.g. Mn(SbF₆)₂,^[19] Ag(XF₆)₂, X = Sb,^[20] Nb,^[21] Ta,^[21] Bi,^[17] Au(SbF₆)₂.^[5] Pertinent crystallographic data are given in Exp. Sect.

A view of the crystal structure of Pd(AsF₆)₂ perpendicular to the slab that contains all palladium atoms in the same plane is shown in Figure 1. Pd atoms are in octahedral environments of fluorine, and PdF₆ octahedra are connected through their vertices to six AsF₆ units on either side of the plane formed by the Pd atoms. There are only van der Waals contacts of fluorine atoms between neighboring slabs and the network is a derivative of the CdCl₂ structural type. The structure can be alternatively described as being derived from the LiSbF₆ type (ordered ReO₃) with ordered

vacancies (□) for half of the cationic sites, i.e. Pd_{0.5}□_{0.5}AsF₆.

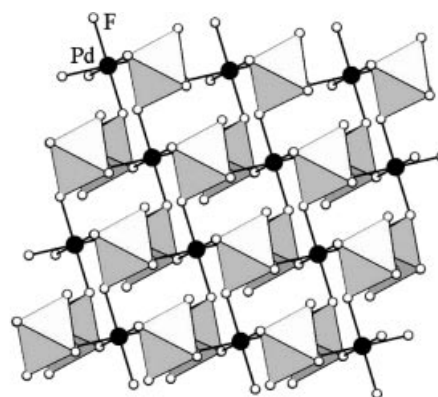


Figure 1. Part of the crystal structure of Pd(AsF₆)₂ perpendicular to the slab containing the palladium atoms.

The six-fold coordination of Pd^{II} in Pd(AsF₆)₂ is different from similar Ag and Au compounds in which, due to the Jahn–Teller effect, the metal octahedral environments are so distorted that coordination around Ag^{II} and Au^{II} is better described as square-planar rather than octahedral. The Pd–F bond lengths [218.3(5)–219.0(5) pm] of hexacoordinated Pd^{II} are slightly longer than the Pd–F bond lengths in PdF₂ [9,22,23] (Figure 2, Table 1).

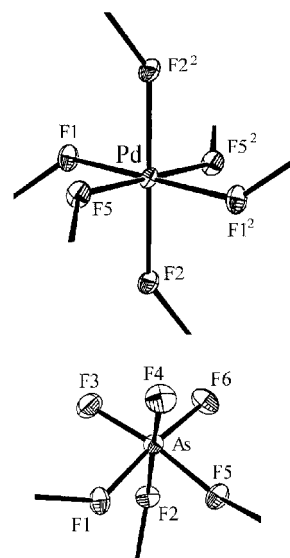


Figure 2. Coordination of the Pd^{II} atom and AsF₆ unit (thermal ellipsoids are shown at the 50% probability level)

The AsF₆[−] anions are highly distorted by their interaction with the cation (Figure 2, Table 1). Consequently three As–F bonds with bridging fluorine atoms are considerably longer [179.8(5), 178.6(5), 176.8(5) pm] than the other three As–F bonds with non-bridging fluorine atoms [166.3(5), 167.9(3), 168.8(5) pm]. From the gross distortion of the AsF₆[−] unit, it is evident that Pd^{II} strongly attracts the fluorine ligands of the surrounding AsF₆ species. The reason

Table 1. Selected bond lengths (pm) and angles (°); symmetry codes used to generate equivalent atoms: $-x, -y, -z$; due to the center of inversion at the Pd center, the coordination of Pd is completed by F1², F2² and F5²

As–F1	179.8(5)	F1–As–F2	84.5(2)	F3–As–F4	95.1(3)
As–F2	176.8(5)	F1–As–F3	88.4(3)	F3–As–F5	172.1(2)
As–F3	167.8(5)	F1–As–F4	89.1(3)	F3–As–F6	96.2(3)
As–F4	168.8(5)	F1–As–F5	84.6(3)		
As–F5	178.6(5)	F1–As–F6	173.5(2)	F4–As–F5	88.4(3)
As–F6	166.3(5)			F4–As–F6	95.0(3)
		F2–As–F3	90.4(3)		
		F2–As–F4	171.5(2)	F5–As–F6	90.6(3)
Pd–F1	218.9(5)	F2–As–F5	85.4(2)	Pd–F1–As	134.7(3)
Pd–F2	219.0(5)	F2–As–F6	90.9(2)	Pd–F2–As	143.5(3)
Pd–F5	218.3(5)			Pd–F5–As	138.0(3)

must be due to the high effective nuclear charge (i.e. the charge density; Z^+/r ratio) of the Pd^{II} cation.

Magnetic Properties of Pd(AsF₆)₂

Because of the peculiar d⁸ electronic configuration of divalent palladium, the Pd^{II} based fluoro-compounds may exhibit either paramagnetic or diamagnetic behavior depending on whether the configuration of the transition element is high-spin or low-spin, respectively. The corresponding coordination numbers are so various that this element has been called an “inorganic chameleon”.^[24] MPdF₄ (M = Ca, Sr, Ba, Pb) and M'MPdF₅ compounds (M' = K, Rb, Cs) are examples of the latter, low-spin case, in which the Pd^{II} has a square planar environment.^[24] In the former case, Pd^{II} exhibits a regular octahedral coordination, as in rutile-type PdF₂ and PdM^{IV}F₆ phases (M^{IV} = Pd, Pt) derived from ReO₃ structures by cationic ordering.^[25] Due to the ordering of Pd electronic orbitals, ferromagnetism occurs in these Pd₂F₆-derived materials. An intermediate case is that of CsPd₂F₅, in which half of the Pd^{II} centers are in a high-spin configuration and the other half in a low-spin state.^[26]

Pd(AsF₆)₂ is paramagnetic and the reciprocal susceptibility follows the Curie–Weiss law with a Weiss constant of -13 K and possible three dimensional ordering below 8 K ($C = 1.56$ and $\mu_{\text{eff}} = 3.53$ B.M.) (Figure 3). The absence of 3D interactions over a large temperature range is in agreement with the structural features. Pd atoms are isolated from each other and there is thus no possible Pd–F–Pd superexchange coupling. The average μ_{eff} is considerably higher than the calculated μ_{eff} considering only spin (2.83 B.M.). Such high values of μ_{eff} were also previously reported for palladium fluorosulfates [Pd(SO₃F)₂: 3.39 B.M.,^[27,28] Pd(M^{IV}(SO₃F)₆): 3.45 B.M. for M = Pd,^[27–29] 3.37 B.M. for M = Pt^[29] and 3.60 B.M. for M = Sn^[29]].

It should be noted that a second Pd^{II} compound with a similar formula, i.e. Pd(SbF₆)₂, is structurally related to Pd(AsF₆)₂. A preliminary crystal structure was reported,^[30] but was incomplete possibly because of twinning of the crystals. The only difference is that in Pd(SbF₆)₂, a dis-

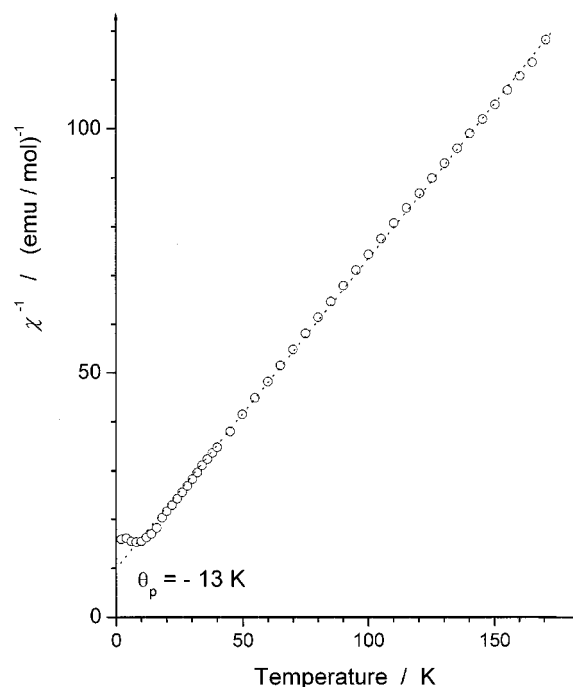


Figure 3. Temperature dependence of the reciprocal magnetic susceptibility of Pd(AsF₆)₂

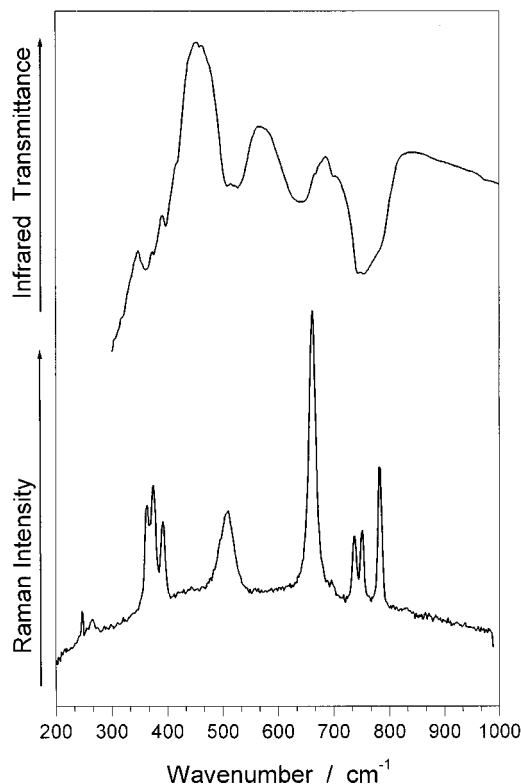


Figure 4. IR and Raman spectra of Pd(AsF₆)₂

ordered distribution of Pd^{II} occurs in all octahedral sites. Magnetic data have been determined^[8,31] over the range 2–82 K (at 82 K Pd(SbF₆)₂ has a $\mu_{\text{eff}} = 3.09$ B.M.).

Vibrational Spectra of Pd(AsF₆)₂

More bands were observed in the vibrational spectra than would be expected for a regular AsF₆[−] anion with O_h symmetry (Figure 4), consistent with a highly distorted AsF₆ octahedral structure in solid Pd(AsF₆)₂. The bands in the region 640–790 cm^{−1} can be assigned to As–F_{terminal} stretching modes. Bands in the region 490–530 cm^{−1}, which are weaker than the stretching ones for terminal fluorine atoms, are typical for species where one fluorine bridges two different atoms,^[1] and can be readily assigned to As–F–Pd stretching modes. Bands below 400 cm^{−1} were assigned to deformation and lattice modes (Table 2).

Table 2. Vibrational spectra of Pd(AsF₆)₂

IR ^[a]	Raman	Partial assignments ^[b]
782(sh)	784(40)	As–F _t stretching modes
759(vs)	751(25)	As–F _t stretching modes
745(vs)		As–F _t stretching modes
	737(20)	As–F _t stretching modes
701(w)	699(5)	As–F _t stretching modes
	662(100)	As–F _t stretching modes
641(s, br)		As–F _t stretching modes
528(s)		As–F–Pd stretching modes
509(s)	509(30)	As–F–Pd stretching modes
	495(sh)	As–F–Pd stretching modes
399(w)	393(20)	deformation modes
377(w)	374(50)	deformation modes
362(w)	366(35)	deformation modes
	264(5)	lattice modes
	246(10)	lattice modes

^[a] Intensities are given in parentheses; w = weak, m = medium, s = strong, vs. = very strong, sh = shoulder. ^[b] F_t = terminal (non-bridging) fluorine atom.

Conclusion

In this study we have investigated the reactions of Pd metal and different Pd compounds (PdF₂, PdO, Pd₂F₆) with AsF₅, with or without elemental fluorine, in liquid aHF. The observed reactions follow the general scheme for the dependence of the generation of low- or high-oxidation states of transition metals on the acid-base properties of the solvent. In neutral aHF, the binary fluoride Pd₂F₆ is formed, whereas acidic aHF favors the metal in a cationic form in the low oxidation state, with formation of Pd(AsF₆)₂. Additionally it was found that the oxidation of Pd metal by fluorine can also partly proceed to Pd(IV) in acidic aHF. It can be concluded that Pd₂F₆ is thermodynamically favorable but kinetically unfavorable relative to Pd(AsF₆)₂.

The partial oxidation of Pd with elemental fluorine to Pd(IV) in acidic or neutral aHF and formation of Pd₂F₆ (Pd^{II}Pd^{IV}F₆) with no further oxidation to PdF₄ is more likely a consequence of unfavorable thermodynamics than kinetics. For the latter, the main reason lies in aHF insoluble Pd₂F₆ which has to be oxidized by fluorine in aHF to

insoluble PdF₄. However, if KrF₂^[15] or ultraviolet photolyzed F₂^[32] are used instead of elemental F₂ in liquid aHF then Pd₂F₆ is quantitatively converted into PdF₄. Treatment of Pd with KrF₂ in aHF is energetically favorable because of the lower heat of atomization of KrF₂ (97.8 kJ·mol^{−1}) in comparison with elemental fluorine (157.7±0.4 kJ·mol^{−1}), making it a better low-temperature source of fluorine atoms.^[33] In the case of the reaction of ultraviolet photolyzed F₂ and Pd in aHF, UV-irradiation provides the energy for the cleavage of the chemical bonds in F₂ and access to atomic fluorine.

The solubility of the reactants and products is not always the governing factor for the generation of the desired oxidation states of transition metals in liquid aHF. For example, elemental fluorine oxidizes MnF₂ in aHF yielding only pure MnF₃. In the presence of a UV source, MnF₂ is completely oxidized by photodissociated F₂ in aHF to MnF₄.^[34] The same thing happens if KrF₂ is used as the oxidizing agent.^[35] However, the suppression of kinetic barriers (insolubility of reactants and products) has a great influence on the preparation of LnF₄ (Ln = Pr, Tb) in liquid aHF. Reactions between LnF₃ and elemental F₂ in aHF at room temperature were incomplete even in the presence of ultraviolet light and gave mixtures of LnF₃ and LnF₄. However when the corresponding Ln oxides were used as starting materials LnF₄ were obtained in a quantitative yields, because the coatings of the reaction products on the surface of the solid reagents were destroyed by gas evolution, thereby accelerating the process.^[36]

When oxidation of Pd by elemental fluorine is carried out in basic aHF (AF/aHF systems; A = alkali metal) with a high concentration of F[−]_(solv), the forming Pd(IV) instantaneously dissolves as PdF₆^{2−}. Although Pd^{II} is formed as an intermediate it has to compete with a stronger Lewis base, i.e. A⁺ for the formation of PdF₆^{2−} salts.

The crystal structure of Pd(AsF₆)₂ confirms the presence of highly distorted AsF₆[−] anions as predicted by vibrational spectroscopy. It is composed of 2D slabs containing Pd atoms in the center and AsF₆ groups on either side. Only van der Waals bonding exists between neighboring slabs. The network can be described as being based on the CdCl₂ structural type or the LiSbF₆ type (ordered ReO₃), with ordered vacancies (□) for half the cationic sites, i.e. Pd_{0.5}□_{0.5}AsF₆. As found by single-crystal X-ray analyses and X-ray powder diffraction, this structure is adopted by most of the known compounds with formula M^{II}(X^VF₆)₂ (M = transition metal; X = As, Sb, Bi, Nb, Ta). Two exceptions are Mn(AsF₆)₂^[37] and Pd(NbF₆)₂.^[38]

The paramagnetic behavior of Pd(AsF₆)₂ is in good agreement with the structural data because no Pd–F–Pd superexchange interaction is possible.

Experimental Section

Apparatus and Reagents: Volatile materials (AsF₅, PF₅, aHF) were manipulated in an all-PTFE vacuum line equipped with PTFE valves. Non-volatile materials were manipulated in a dry-box (M.

Braun). The residual water in the atmosphere within the dry-box never exceeded 1 ppm. The reactions were carried out in translucent fluorocarbon polymer (FEP) reaction vessels (height 250–300 mm with inner diameter 15.5 mm and outer diameter 18.75 mm) equipped with PTFE body valves and PTFE coated stirring bars. Reaction vessels combined from two FEP tubes in a T-shape manner and equipped with PTFE body valves were used in some experiments. Each reaction vessel was pre-treated with F_2 (to about 1 bar) for several hours before use.

Pd black (Alfa Products, 99.9%), Pd black (Aldrich, 99.9%), Pd gray (Johnson Matthey & Co-limited, 99.9%), Pd gray (Merck, 99.9%), Pd sponge (Aldrich, 99.9%), PdO (Cerac Incorporated, 99.99%), and KF (Ventron, 99.9%) were used as supplied. AsF_5 was synthesized by pressure fluorination of arsenic trioxide with elemental fluorine in a nickel reactor at 573 K as described for the synthesis of PF_5 .^[39] KPF_6 was prepared from KF and PF_5 in aHF. The lilac rutile form of PdF_2 was prepared as described.^[40] Fluorine was used as supplied (Solvay, 99.98%). Anhydrous HF (Praxair, 99.9%) was treated with K_2NiF_6 for several hours prior to use.

CAUTION: aHF, AsF_5 , and PF_5 should only be handled in a well-ventilated hood, and protective clothing should be worn at all times!

Instrumentation: Infrared spectra were recorded on a Perkin–Elmer FTIR 1710 spectrometer on powdered samples between AgCl plates in a leak-tight brass cell. Raman spectra were recorded on a Renishaw Raman Imaging Microscope System 1000, with a He–Ne laser of wavelength 632.8 nm. X-ray powder diffraction patterns were obtained using the Debye–Scherrer technique with Ni-filtered $Cu-K_\alpha$ radiation. Samples were loaded into quartz capillaries (0.3 mm) in a dry-box.

Chemical Analyses: Palladium was determined by complexometric titration;^[41–43] total fluoride ion content was determined with a fluoride ion selective electrode;^[44,45] AsF_6^- species were determined gravimetrically as insoluble tetraphenylarsonium salts;^[46,47] arsenic was determined by the ICP method.^[48] The results of chemical analyses are given in mass percentages.

Syntheses

General Procedure: Starting materials were loaded into an FEP reaction vessel in a glove box. aHF and, when necessary, AsF_5 were condensed onto solid reactants at 77 K, which were then brought to room temperature. Fluorine was added when needed. The reaction mixtures were vigorously agitated and after some time volatiles were pumped away. Isolated products were characterized by mass balance, chemical analysis, vibrational spectroscopy, X-ray powder diffraction patterns (XRPD-pattern) and/or magnetic measurements.

Reaction between Pd and F_2 in aHF: Reaction mixture: Pd (0.242 g, 2.27 mmol) and F_2 (13.99 mmol) in aHF (6 mL). After 4 days no visible change was observed (colorless liquid was present above a black solid). Final mass: 0.401 g (calcd. for Pd_2F_6 : 0.371 g). XRPD-pattern and Raman spectrum (563 cm^{-1} , 281 cm^{-1} and 213 cm^{-1}) corresponded to Pd_2F_6 . Pd_2F_6 (326.8): calcd. F 34.88, Pd 65.12; found F 34.6, Pd 63.9.

Reaction between PdO and F_2 in aHF: Reaction mixture: PdO (0.191 g, 1.56 mmol) and F_2 (12.92 mmol) in aHF (4 mL). After 48 days no visible change was observed (colorless liquid was present above a black solid). Pd_2F_6 (326.8): calcd. F 34.88; found F 23.4. XRPD-pattern showed a mixture of PdO and Pd_2F_6 .

Reaction between PdF_2 and F_2 in aHF: Reaction mixture: rutile form of PdF_2 (0.275 g, 1.90 mmol) and F_2 (12.92 mmol) in aHF (4 mL). After 13 days, the liquid was colorless and starting PdF_2 remained as an insoluble brown solid, characterized by XRPD-pattern. PdF_2 (144.4): calcd. F 26.32, Pd 73.68; found F 26.9, Pd 72.1.

Reactions between Pd and AsF_5 in aHF: Two experiments were carried out. In the first experiment, a reaction mixture of Pd (0.110 g) and AsF_5 (2.000 g) in aHF (4 mL) was prepared. After 3 days a green-blue solution was observed above unchanged Pd metal. The Raman spectrum of the solution showed a strong band at 703 cm^{-1} , which could be attributed to $As_2F_{11}^-$. After 42 days the volatile components were pumped away. The XRPD-pattern of the isolated solid showed only Pd metal. Chemical analysis showed 4.78% As in the isolated solid.

In the second experiment a solution of AsF_5 (2.000 g) in aHF (3 mL) was treated with 4 bar of hydrogen. After one day of intensive stirring the solution was cooled to 77 K, and volatile components were pumped away. The mixture of AsF_5 /aHF was then brought to room temperature and condensed onto Pd metal (0.118 g, 1.11 mmol). The Raman spectrum of the liquid phase showed a strong band at 703 cm^{-1} . After 42 days the liquid phase was still colorless. The XRPD-pattern of the isolated solid showed it to consist of metallic Pd. Pd (106.4): calcd. Pd 100; found Pd 98.2.

Reaction between PdO and AsF_5 with and without F_2 in aHF: Reaction mixture: PdO (0.182 g, 1.49 mmol) and AsF_5 (11.77 mmol) in aHF (4 mL). The Raman spectrum of the solution showed a strong band at 703 cm^{-1} . After 8 days the liquid phase was still colorless. Because there was no sign of reaction, F_2 (1.96 mmol) was added to the reaction vessel. The liquid phase became green-blue over few hours. Within 13 days a clear green-blue solution was obtained. Volatiles were pumped away at 253 K. Final mass of isolated green solid: 0.799 g [calcd. for $Pd(AsF_6)_2$: 0.726 g]. $Pd(AsF_6)_2$ (484.2): calcd. Pd 21.97; F 47.09; As 30.94; AsF_6 78.03; found Pd 21.4; F 46.3; As 33.3; AsF_6 76.0 [corresponding to molar ratio: $n(Pd):n(As):n(AsF_6):n(F) = 1.0:2.2:2.0:12.1$].

Reaction between PdF_2 and AsF_5 in aHF: Immediately after warming to room temperature, a reaction mixture of PdF_2 (0.270 g, 1.87 mmol) and AsF_5 (5.90 mmol) in aHF (4 mL) became green-blue in color. After three days, some of the volatiles were pumped away at room temperature until 1 mL of solution was left. Finally, all volatiles were pumped away over 6 days at 243 K. Final mass of the green solid: 0.913 g, calcd. for $Pd(AsF_6)_2$: 0.906 g. $Pd(AsF_6)_2$ (484.2): calcd. Pd 21.97, F 47.09, AsF_6 78.03; found Pd 21.7, F 46.3, AsF_6 76.6.

Reaction between Pd_2F_6 and AsF_5 in aHF: Reaction mixture: Pd_2F_6 (0.138 g, 0.84 mmol) and AsF_5 (3.53 mmol) in aHF (6 mL). After 6 days the liquid phase was still colorless, and the insoluble solid was black. The XRPD-pattern and Raman spectrum (563 , 283 and 215 cm^{-1}) of the isolated solid showed only starting Pd_2F_6 . Pd_2F_6 (326.8): calcd. F 34.88; found F 34.9.

Reactions between Pd and AsF_5 in aHF in the Presence of Fluorine: Many experiments were performed with different forms of Pd. Only two typical ones will be described. Reaction mixture: Pd (0.292 g, 2.74 mmol), AsF_5 (7.06 mmol) and F_2 (4.95 mmol) in aHF (10 mL). After one hour the color of the solution became green–blue. After 5 days a clear green-blue solution was obtained. Volatiles were pumped away at room temperature. The final mass of isolated grayish–green solid was 1.246 g, corresponding to a

molar ratio $n(\text{PdF}_2):n(\text{AsF}_5) = 1:1.87$. $\text{Pd}(\text{AsF}_6)_2$ (484.2): calcd. Pd 21.97, F 47.09, As 30.94, AsF₆ 78.03; found Pd 23.2, F 45.3, As 30.6, AsF₆ 76.1 [corresponding to molar ratio $n(\text{PdF}_2):n(\text{AsF}_5) = 1:1.87$]. In other experiments different final molar ratios $n(\text{PdF}_2):n(\text{AsF}_5)$ were obtained giving “ $\text{PdF}_x(\text{AsF}_6)_{2-x}$ ” where $0 < x \leq 1$ depending on the temperature and time of isolation and vacuum conditions. Reaction mixture: Pd (0.281 g, 2.64 mmol), AsF₅ (20.56 mmol) and F₂ (3.53 mmol) in aHF (8 mL). After 5 days a clear green–blue solution was obtained. Volatiles were pumped away for 10 days at 253 K. The isolated solid product was green. $\text{Pd}(\text{AsF}_6)_2$ (484.2): calcd. Pd 21.97, F 47.09, As 30.94, AsF₆ 78.03; found Pd 21.4, F 46.1, As 33.8, AsF₆ 77.3 [corresponding to molar ratio $n(\text{Pd}):n(\text{As}):n(\text{AsF}_6):n(\text{F}) = 1.0:2.2:2.0:12.1$].

Reaction between Pd and AsF₅ in aHF in the Presence of a Large Excess of Fluorine: Reaction mixture: Pd (0.326 g, 3.06 mmol), AsF₅ (25.15 mmol) and F₂ (11.95 mmol) in aHF (8 mL). After bringing the reaction mixture to room temperature, the color of the liquid phase changed to green–blue. After 10 days a clear green–blue solution was visible above an insoluble black solid. The solution was decanted. The mass of black solid was 0.359 g. Its Raman spectrum (565, 291 and 219 cm^{−1}) showed only Pd₂F₆. The XRPD-pattern of green solid isolated from decanted solution showed only $\text{Pd}(\text{AsF}_6)_2$.

Reaction between Pd₂F₆ and H₂ in aHF: Pd₂F₆ (0.239 g, 1.46 mmol) was suspended in HF (7 mL) and agitated intensively at room temperature. Immediately after addition of hydrogen the sample deposited on the bottom of the reaction vessel despite intensive stirring. The final pressure of hydrogen was 3.7 bar. After one day volatiles were pumped away at room temperature. Final mass: 0.169 g (calcd. for Pd: 0.155 g). Pd (106.4): calcd. Pd 100; found Pd 97.8. The XRPD-pattern showed Pd metal.

Reduction and Oxidation of Solvated Pd²⁺ Dissolved in AsF₅/aHF: A clear green blue solution was prepared from Pd (0.133 g, 1.26 mmol), AsF₅ (3.700 g, 21.78 mmol) and F₂ (1.50 mmol) in aHF (8 mL). The excess fluorine was pumped away at 77 K. After addition of 2 bar of hydrogen at room temperature, the liquid phase became colorless over 10 minutes. A metallic, shiny solid precipitated on the walls of reaction vessel. Volatiles were pumped away at room temperature. Final mass: 0.167 g. Chemical analysis: % Pd, 92.5, % As, 4.2. The XRPD-pattern showed only Pd metal.

A green blue solution of Pd metal was prepared as above. After addition of elemental fluorine, a black solid started to precipitate. The amount of insoluble solid increased with time and the intensity of the green–blue color of the liquid phase decreased. The XRPD-pattern of the isolated solid showed only Pd₂F₆.

Attempted Synthesis of PdFAsF₆: A T-shaped FEP reactor with two PTFE valves as described before^[49] was loaded with Pd (0.155 g, 1.46 mmol) in one arm and KPF₆ (0.266 g, 1.46 mmol) in the other. aHF (about 4 mL), AsF₅ (2 g) and F₂ (1.60 mmol) were condensed onto the Pd and in the other arm aHF (3 mL) was condensed onto KPF₆, yielding a colorless solution. After one day the Pd metal completely dissolved, yielding a blue–green solution. Volatiles were pumped away at 253 K and fresh aHF was added. The solution of KPF₆ in aHF was slowly poured onto the clear solution of $\text{Pd}(\text{AsF}_6)_2$ in aHF. A light–brown solid immediately precipitated. After two days a green–blue solution was visible above the light–brown solid. The solution was decanted. The XRPD-pattern of the insoluble brown solid corresponded to the low-temperature form of PdF₂.^[9] The XRPD-pattern and Raman spectrum of the solid

precipitated from the decanted solution showed a mixture of KAsF₆ and $\text{Pd}(\text{AsF}_6)_2$.

Preparation of Single-Crystals of $\text{Pd}(\text{AsF}_6)_2$ and Structure Determination: The crystal structure of $\text{Pd}(\text{AsF}_6)_2$ was first determined on our single-crystals with the help of Dr. H. Borrmann, Max Planck Institut für Chemische Physik fester Stoffe, Dresden, Germany. Later the determination of the crystal structure of $\text{Pd}(\text{AsF}_6)_2$ was repeated on new crystals. All crystallographic data presented in this paper are from repeated crystal structure determinations.

Single-crystals of $\text{Pd}(\text{AsF}_6)_2$ were prepared by solvothermal syntheses. The reaction between Pd (0.110 g, 1.03 mmol), AsF₅ (1.5 g, 8.83 mmol), aHF (0.050 g) and F₂ (1.5 mmol) was carried out in a special stainless steel autoclave with a PTFE liner (*V* = 6 mL). After entering all reactants into the autoclave it was heated to 393 K for 43 days. After cooling to ambient temperature all volatiles were quickly pumped away. A large piece of brown solid was found inside. When it was broken up, blue–green crystals of $\text{Pd}(\text{AsF}_6)_2$ were found inside. Single-crystals were selected in a dry-box and mounted in 0.3 mm quartz capillaries.

Single-crystal data from $\text{Pd}(\text{AsF}_6)_2$ were collected on a Mercury CCD area detector coupled with a Rigaku AFC7S diffractometer using monochromated MoK_α radiation. Data were corrected for Lorentz, polarization, and absorption effects and processed using the Rigaku Crystalclear software suite program package.^[50] The structure was solved by direct methods^[51] and expanded using Fourier techniques. Some details of the single-crystal data collection, data processing, and refinement are given in Table 3. Further details of the crystal-structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-

Table 3. Crystal data and structure refinement for $\text{Pd}(\text{AsF}_6)_2$

Formula	$\text{Pd}(\text{AsF}_6)_2$
Crystal system	triclinic
Space group	$P\bar{1}$ (No.2)
Unit cell dimensions (pm,°)	<i>a</i> = 500.9(5) <i>b</i> = 538.3(5) <i>c</i> = 864.9(9) α = 74.46(3) β = 89.97(4) γ = 62.47(2) 0.1972(3)
<i>V</i> (nm ³)	4.079
<i>D</i> _{calcd.} (gcm ^{−3})	1
<i>Z</i>	1
Molecular mass (gmol ^{−1})	484.24
Wavelength (pm)	71.069
Temperature (K)	293(2)
θ range for data collection (°)	2.47 ≤ θ ≤ 29.00
Index ranges	−6 ≤ <i>h</i> ≤ 6, −6 ≤ <i>k</i> ≤ 6, −6 ≤ <i>l</i> ≤ 11
Reflections collected	898
Independent reflections	796 (<i>R</i> _{int} = 0.0256)
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	762
Refinement method	Full matrix least-squares on <i>F</i> ²
Data/restraints/parameters	796/0/70
Absorption correction	multi-scan
Absorption coefficient (mm ^{−1})	10.864
Goodness-of-fit on <i>F</i> ²	1.061
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0615, <i>wR</i> 2 = 0.1620
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0602, <i>wR</i> 2 = 0.1599

[a] $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}$, $GOF = \Sigma [w(F_o^2 - F_c^2)^2 / (N_o - N_p)]^{1/2}$, where *N*_o = no. of reflections and *N*_p = no. of refined parameters.

Leopoldshafen, Germany, on quoting the depository number CSD-413415.

Magnetic Measurements: Cylindrical screw-capped sample containers ($V \approx 0.5$ mL, $m \approx 0.250$ mg) for magnetic measurements of $\text{Pd}(\text{AsF}_6)_2$ were made of Kel-F (polytrifluorochloroethylene) and were additionally tightened with PTFE gaskets. Prior to their use, both the container and Kel-F packing tool were made passive with elemental fluorine. The field dependence of the magnetization was measured for various temperatures in the 4.2–300 K range using a SQUID magnetometer (MPMS-5S, Quantum Design).

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