# Palladium Chemistry in Anhydrous HF/AsF$_5$ Superacid Medium

**Zoran Mazej,*[a] Primož Benkič,[a] Alain Tressaud,[b] and Boris Žemva[a]**

Pd metal dissolves in anhydrous HF (aHF) acidified with AsF$_5$ in the presence of F$_2$ at $\approx$298 K to give a blue-green solution from which green Pd(AsF$_6$)$_2$ can be isolated. The latter was also prepared by the interaction of PdF$_2$ and AsF$_5$ in aHF or by the reaction between PdO and F$_2$ in aHF acidified with AsF$_5$. Powdered Pd(AsF$_6$)$_2$ slowly loses AsF$_5$ in a dynamic vacuum. It can therefore be isolated from solution at $T < 253$ K. Single-crystals of Pd(AsF$_6$)$_2$ were prepared by solvothermal synthesis from a Pd/AsF$_5$/F$_2$/aHF mixture at 393 K. Pd(AsF$_6$)$_2$ is triclinic with $a = 500.9(5)$, $b = 538.3(5)$, $c = 864.9(9)$ pm, $\alpha = 74.46(3)$, $\beta = 89.97(4)$, $\gamma = 62.47(2)°$, $V = 0.1972(3)$ nm$^3$, and $Z = 1$, space group $P\bar{1}$ (No. 2). The six-coordinate Pd atoms (coordinated with fluorine) are well sep-

arated by isolated AsF$_6$ units. In the 2–175 K temperature range Pd(AsF$_6$)$_2$ follows the Curie–Weiss law with $\mu_{eff} = 3.53$ B.M., $T_n = 8$ K and $\theta_p = -13$ K. Because of cation-anion interactions, the AsF$_6^-$ 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 F$_2$ in neutral aHF yielded Pd$_2$F$_6$. No reaction was observed between Pd, PdO or Pd$_2$F$_6$ and AsF$_5$ in aHF. All attempts to prepare PdFAsF$_6$ were unsuccessful.

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## Introduction

Ususally, 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. AsF$_5$) 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 PdF$_6^{2-}$ anion (Li$_2$PdF$_6$,[8] K$_2$PdF$_6$,[8] (NH$_4$)$_2$PdF$_6$ [7]), whereas in acidic aHF (acidified with SbF$_5$) the final product of oxidation, i.e. Pd(SbF$_6$)$_2$,[8] contained a low-oxidation state Pd$^{II}$ cation. Our preliminary results showed that clear blue-green solutions of the Pd$^{II}$ salt [Pd(AsF$_6$)$_2$], when treated with alkali fluoride in aHF, gave a light-brown precipitate of a new variety of PdF$_2$ (low-temperature form),[9] while the same procedure on Pd(SbF$_6$)$_2$ gave the previously known lilac rutile-type form of PdF$_2$.[8] For that reason we decided to study palladium chemistry in AsF$_5$/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, PdF$_2$ and Pd$_2$F$_6$) are treated with aHF acidified with AsF$_5$ (a Lewis acid weaker than SbF$_5$) in the presence or absence of elemental fluorine. The results of investigations of palladium chemistry in neutral aHF are also reported.
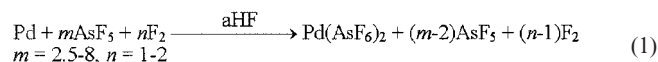
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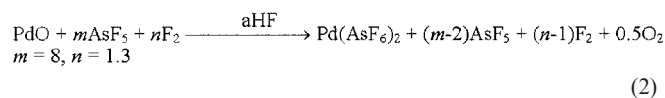
## Results and Discussion

### Syntheses

AsF$_5$ is able to oxidize 3$d$-metals at room temperature using AsF$_3$ or anhydrous hydrogen fluoride (aHF) as the solvent, giving $M$(AsF$_6$)$_2$, $M$FAsF$_6$ or $M$(AsF$_6$)$_2$·2AsF$_3$ 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 AsF$_5$. In the superacidic system AsF$_5$/aHF, palladium was slowly oxidized and finally completely dissolved yielding a green-blue solution of solvated Pd$^{2+}$ cations, from which green Pd(AsF$_6$)$_2$ was isolated [Equation (1)]

$$Pd + m\text{AsF}_5 + n\text{F}_2 \xrightarrow[m = 2.5\text{-}8, \, n = 1\text{-}2]{\text{aHF}} \text{Pd(AsF}_6)_2 + (m\text{-}2)\text{AsF}_5 + (n\text{-}1)\text{F}_2 \quad (1)$$

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 AsF$_5$ in aHF we observed a green-blue solution, indicating a possible reaction. Later we discovered, however, that the reason lay in impure AsF$_5$ contaminated by traces of fluorine. When superacid AsF$_5$/aHF was first treated with hydrogen and then allowed to react with palladium, no such coloring of the liquid phase was observed.
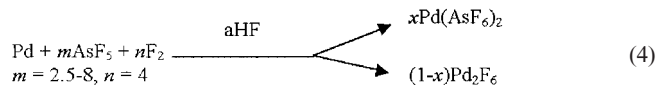
PdO does not dissolve in an AsF$_5$/aHF superacidic system, contrary to some other oxides of 3$d$- and 5$f$-transition metals which can yield oxonium salts.[11,12] On addition of elemental fluorine to a suspension of PdO in AsF$_5$/aHF, the reaction proceeds with formation of a green-blue solution from which Pd(AsF$_6$)$_2$ can be isolated [Equation (2)].
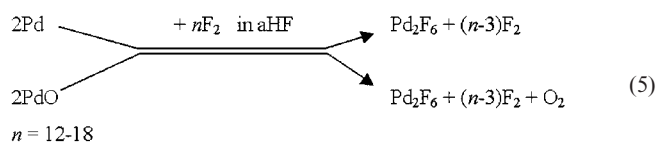
$$PdO + m\text{AsF}_5 + n\text{F}_2 \xrightarrow[m = 8, \, n = 1.3]{\text{aHF}} \text{Pd(AsF}_6)_2 + (m\text{-}2)\text{AsF}_5 + (n\text{-}1)\text{F}_2 + 0.5\text{O}_2 \quad (2)$$

Pd(AsF$_6$)$_2$ can be prepared directly by the reaction between PdF$_2$ and AsF$_5$ in aHF [Equation (3)].

$$PdF_2 + m\text{AsF}_5 \xrightarrow[m = 3]{\text{aHF}} \text{Pd(AsF}_6)_2 + (m\text{-}2)\text{AsF}_5 \quad (3)$$
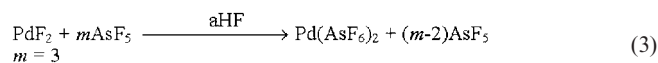
For the first two reactions [Equations (1) and (2)] the amount of fluorine is very important. In the literature it has been reported that addition of fluorine to a solution of AgF$_2$ in AsF$_5$/aHF causes the partial oxidation of Ag$^{II}$ to Ag$^{III}$ and formation of (Ag$^{II}$F)$_2$(Ag$^{III}$F$_4$)AsF$_6$.[13] On prolonged exposure to F$_2$ of the highly aHF$-$soluble Au(SbF$_6$)$_2$, part of the Au$^{II}$ is oxidized to Au$^{III}$, yielding mixed$-$valence, poorly soluble Au$^{II}$(SbF$_6$)$_2$Au$^{II}$-(Au$^{III}$F$_4$)$_2$.[5] If the excess of fluorine in reactions (1) and (2) is too great, black aHF$-$insoluble mixed-oxidation state Pd$_2$F$_6$, i.e. Pd$^{II}$(Pd$^{IV}$F$_6$),[14] is formed besides aHF$-$soluble Pd(AsF$_6$)$_2$ [Equation (4)].

$$Pd + m\text{AsF}_5 + n\text{F}_2 \xrightarrow{\text{aHF}} \begin{array}{c} x\text{Pd(AsF}_6)_2 \\ (1\text{-}x)\text{Pd}_2\text{F}_6 \end{array} \quad (4)$$
$$m = 2.5\text{-}8, \, n = 4$$

The precipitation of black Pd$_2$F$_6$ also occurred when fluorine was added to a clear green$-$blue solution of solvated Pd$^{2+}$ in AsF$_5$/aHF. Reactions between Pd or PdO and F$_2$ in neutral aHF also yielded Pd$_2$F$_6$ [Equation (5)].

$$\begin{array}{c} 2\text{Pd} \\ 2\text{PdO} \end{array} \xrightarrow{+ n\text{F}_2 \text{ in aHF}} \begin{array}{c} \text{Pd}_2\text{F}_6 + (n\text{-}3)\text{F}_2 \\ \text{Pd}_2\text{F}_6 + (n\text{-}3)\text{F}_2 + \text{O}_2 \end{array} \quad (5)$$
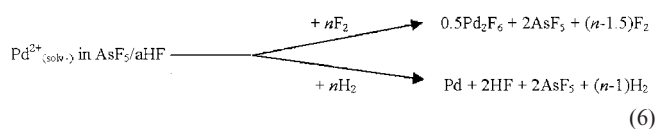$$n = 12\text{-}18$$

Even when PdO and F$_2$ in aHF were left to react for a longer time (48 days) than Pd and F$_2$ in aHF (4 days), unchanged PdO was still present in the solid and only $\approx$60 mol % of starting PdO was converted into Pd$_2$F$_6$. It is also worth noting that there was no sign of any reaction between PdF$_2$ and F$_2$ in aHF, even after several days, probably due to kinetic reasons.

The formation of Pd$_2$F$_6$ 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 (KrF$_2$) than fluorine in neutral or acid aHF (acidified with AsF$_5$), all Pd is oxidized to Pd$^{IV}$F$_4$.[15] The main driving forces for the formation of Pd(AsF$_6$)$_2$ or PdPdF$_6$ are the fluoride ion affinities of AsF$_5$ (PdF$_4$) and the lattice energy differences between PdF$_2$ and the complex fluoroanion salts Pd(AsF$_6$)$_2$ (PdPdF$_6$). Since even PdF$_4$ prepared in situ does not react with AsF$_5$ [15] and precipitates on addition of AsF$_5$ to aHF solutions of PdF$_6^{2-}$ alkali metal salts,[16] it can be concluded that the Lewis acidity (fluoroacidity or fluoride ion affinity) of PdF$_4$ is weaker than that of AsF$_5$. The driving force for the formation of Pd$_2$F$_6$ (PdF$_2$+PdF$_4$), despite the presence of the stronger fluoro acid AsF$_5$, is its high lattice energy. This explains why AsF$_5$ is not able to precipitate PdF$_4$ from Pd$_2$F$_6$ although it has a higher fluoride ion affinity than PdF$_4$.

Solvated Pd$^{II}$ in green-blue solutions of Pd(AsF$_6$)$_2$ can, on the other hand, be easily oxidized or reduced, yielding finely powdered Pd$_2$F$_6$ or Pd metal, respectively [Equation (6)].

$$Pd^{2+}_{(solv.)} \text{ in AsF}_5/\text{aHF} \begin{array}{c} \xrightarrow{+ n\text{F}_2} 0.5\text{Pd}_2\text{F}_6 + 2\text{AsF}_5 + (n\text{-}1.5)\text{F}_2 \\ \xrightarrow{+ n\text{H}_2} \text{Pd} + 2\text{HF} + 2\text{AsF}_5 + (n\text{-}1)\text{H}_2 \end{array} \quad (6)$$

Additionally it was found that Pd$_2$F$_6$ can also be reduced by hydrogen in aHF yielding powdered Pd metal [Equation (7)].

$$Pd_2F_6 + nH_2 \xrightarrow{aHF} 2Pd + 6HF + (n\text{-}3)H_2 \qquad (7)$$
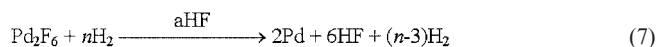
To prepare pure $Pd(AsF_6)_2$ according to reactions (1), (2) and (3), the temperature of recovery from solution is important. It was found that $Pd(AsF_6)_2$ releases $AsF_5$ in a dynamic vacuum. Pure $Pd(AsF_6)_2$ can be isolated from solution in aHF by pumping away volatiles at temperatures lower than 253 K. At room temperature, the isolated products had varied compositions "$PdF_x(AsF_6)_{2-x}$" with $0 < x \leq 1$ 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 $Pd(AsF_6)_2$. Even the X−ray powder pattern of the phase close to a "$PdFAsF_6$" composition was the same as that of $Pd(AsF_6)_2$. We also tried to prepare $PdFAsF_6$ by displacing a weak acid from its alkali metal salt, similar to that reported for $AgFBiF_6$ from $Ag(BiF_6)_2$ [17] but, instead of $PdFAsF_6$, a mixture of $Pd(AsF_6)_2$ and a low-temperature modification of $PdF_2$ [9] was always obtained [Equation (8)].

$$Pd(AsF_6)_2 + KPF_6 \xrightarrow{aHF} 0.5Pd(AsF_6)_2 + 0.5PdF_2 + KAsF_6 + PF_5 \qquad (8)$$
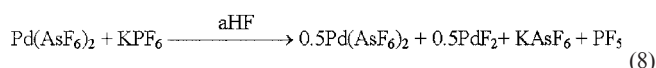
On the basis of these results we conclude that phases with compositions $PdF_x(AsF_6)_{2-x}$ ($0 < x \leq 1$) are mixtures of $Pd(AsF_6)_2$ and $PdF_2$ and not mixtures of $Pd(AsF_6)_2$ and $PdFAsF_6$. The possible preparation and existence of $PdFAsF_6$ is thus still in question. The instability of $Pd(AsF_6)_2$ in a dynamic vacuum could be a consequence of the inadequate fluoroacidity of $AsF_5$. When a stronger fluoroacid $SbF_5$ (FIA[$SbF_5$,g] $\approx$ −506 (± 63) kJ/mol)[18] was used instead of $AsF_5$ (FIA[$AsF_5$,g] $\approx$ −421 (± 22) kJ/mol)[18] the resultant $Pd(SbF_6)_2$ was stable at room temperature.[8] However care must be exercised in this type of comparison, in that the relative volatilities of $AsF_5$ and $SbF_5$ are also important factors in the stabilities of the resultant $Pd(AsF_6)_2$ and $Pd(SbF_6)_2$.

## Crystal Structure of $Pd(AsF_6)_2$

$Pd(AsF_6)_2$ crystallizes in the same structural category as many other compounds obtained in the systems $MF_2/XF_5$ ($M$ = transition metal, $XF_5$ = Lewis acid), e.g. $Mn(SbF_6)_2$,[19] $Ag(XF_6)_2$, $X$ = Sb,[20] Nb,[21] Ta,[21] Bi,[17] $Au(SbF_6)_2$.[5] Pertinent crystallographic data are given in Exp. Sect.

A view of the crystal structure of $Pd(AsF_6)_2$ 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 $PdF_6$ octahedra are connected through their vertices to six $AsF_6$ 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 $CdCl_2$ structural type. The structure can be alternatively described as being derived from the $LiSbF_6$ type (ordered $ReO_3$) with ordered

vacancies ($\square$) for half of the cationic sites, i.e. $Pd_{0.5}\square_{0.5}AsF_6$.
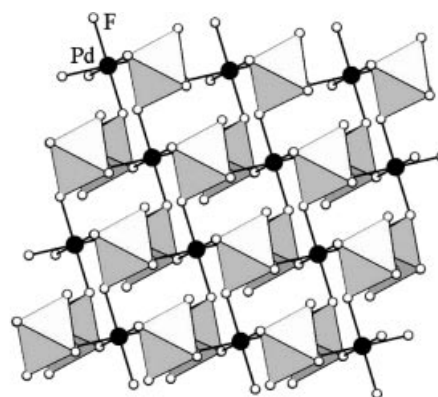


Figure 1. Part of the crystal structure of $Pd(AsF_6)_2$ perpendicular to the slab containing the palladium atoms.

The six-fold coordination of $Pd^{II}$ in $Pd(AsF_6)_2$ 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 $PdF_2$ [9,22,23] (Figure 2, Table 1).
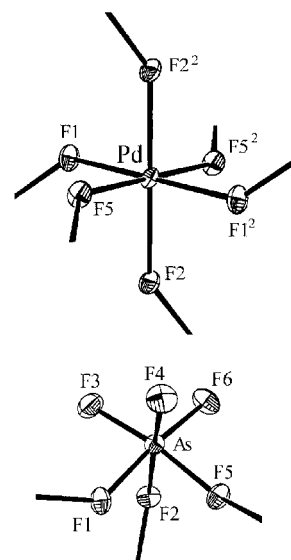


Figure 2. Coordination of the $Pd^{II}$ atom and $AsF_6$ unit (thermal ellipsoids are shown at the 50% probability level)

The $AsF_6^-$ 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 $AsF_6^-$ unit, it is evident that $Pd^{II}$ strongly attracts the fluorine ligands of the surrounding $AsF_6$ 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 $F1^2$, $F2^2$ and $F5^2$

| | | | | | |
|---|---|---|---|---|---|
| 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–F2 | 219.0(5) | F2–As–F6 | 90.9(2) | Pd–F1–As | 134.7(3) |
| Pd–F5 | 218.3(5) | | | Pd–F2–As | 143.5(3) |
| | | | | 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 $d^8$ 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] $MPdF_4$ (M = Ca, Sr, Ba, Pb) and $M'MPdF_5$ 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 $PdF_2$ and $PdM^{IV}F_6$ phases ($M^{IV}$ = Pd, Pt) derived from $ReO_3$ structures by cationic ordering.[25] Due to the ordering of Pd electronic orbitals, ferromagnetism occurs in these $Pd_2F_6$-derived materials. An intermediate case is that of $CsPd_2F_5$, in which half of the $Pd^{II}$ centers are in a high-spin configuration and the other half in a low–spin state.[26]

$Pd(AsF_6)_2$ 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 $\mu_{eff} = 3.53$ 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 $\mu_{eff}$ is considerably higher than the calculated $\mu_{eff}$ considering only spin (2.83 B.M). Such high values of $\mu_{eff}$ were also previously reported for palladium fluorosulfates [$Pd(SO_3F)_2$: 3.39 B.M.,[27,28] $Pd(M^{IV}(SO_3F)_6$]: 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. $Pd(SbF_6)_2$, is structurally related to $Pd(AsF_6)_2$. A preliminary crystal structure was reported,[30] but was incomplete possibly because of twinning of the crystals. The only difference is that in $Pd(SbF_6)_2$, a dis-
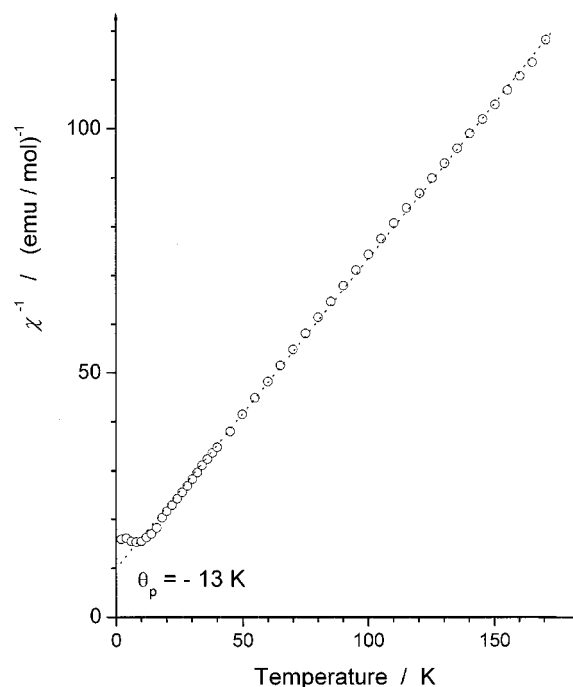
Figure 3. Temperature dependence of the reciprocal magnetic susceptibility of $Pd(AsF_6)_2$
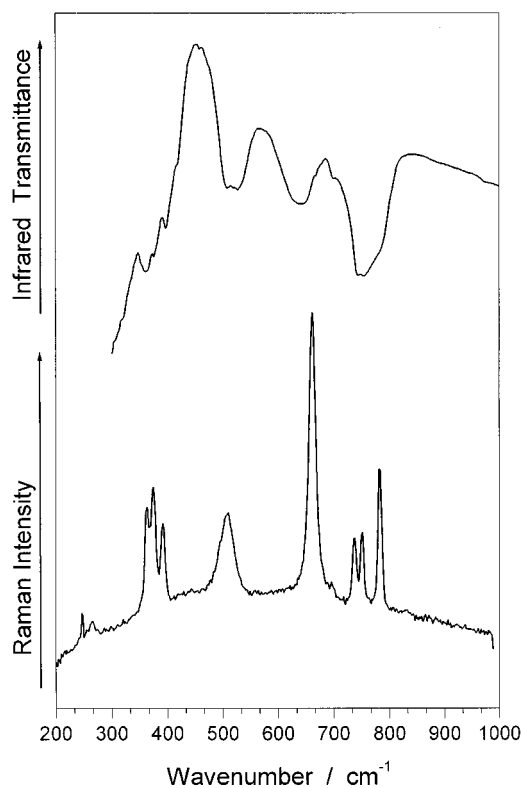
Figure 4. IR and Raman spectra of $Pd(AsF_6)_2$

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 $Pd(SbF_6)_2$ has a $\mu_{eff} = 3.09$ B.M.).

## Vibrational Spectra of Pd(AsF$_6$)$_2$

More bands were observed in the vibrational spectra than would be expected for a regular AsF$_6^-$ anion with O$_h$ symmetry (Figure 4), consistent with a highly distorted AsF$_6$ octahedral structure in solid Pd(AsF$_6$)$_2$. 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(AsF$_6$)$_2$

| 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 (PdF$_2$, PdO, Pd$_2$F$_6$) with AsF$_5$, 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 Pd$_2$F$_6$ is formed, whereas acidic aHF favors the metal in a cationic form in the low oxidation state, with formation of Pd(AsF$_6$)$_2$. 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 Pd$_2$F$_6$ is thermodynamically favorable but kinetically unfavorable relative to Pd(AsF$_6$)$_2$.

The partial oxidation of Pd with elemental fluorine to Pd(IV) in acidic or neutral aHF and formation of Pd$_2$F$_6$ (Pd$^{II}$Pd$^{IV}$F$_6$) with no further oxidation to PdF$_4$ is more likely a consequence of unfavorable thermodynamics than kinetics. For the latter, the main reason lies in aHF insoluble Pd$_2$F$_6$ which has to be oxidized by fluorine in aHF to

insoluble PdF$_4$. However, if KrF$_2$ [15] or ultraviolet photolyzed F$_2$ [32] are used instead of elemental F$_2$ in liquid aHF then Pd$_2$F$_6$ is quantitatively converted into PdF$_4$. Treatment of Pd with KrF$_2$ in aHF is energetically favorable because of the lower heat of atomization of KrF$_2$ (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 F$_2$ and Pd in aHF, UV-irradiation provides the energy for the cleavage of the chemical bonds in F$_2$ 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 MnF$_2$ in aHF yielding only pure MnF$_3$. In the presence of a UV source, MnF$_2$ is completely oxidized by photodissociated F$_2$ in aHF to MnF$_4$.[34] The same thing happens if KrF$_2$ 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 LnF$_4$ (Ln = Pr, Tb) in liquid aHF. Reactions between LnF$_3$ and elemental F$_2$ in aHF at room temperature were incomplete even in the presence of ultraviolet light and gave mixtures of LnF$_3$ and LnF$_4$. However when the corresponding Ln oxides were used as starting materials LnF$_4$ 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 (*A*F/aHF systems; *A* = alkali metal) with a high concentration of F$^-_{(solv)}$, the forming Pd(IV) instantaneously dissolves as PdF$_6^{2-}$. Although Pd$^{II}$ is formed as an intermediate it has to compete with a stronger Lewis base, i.e. *A*$^+$ for the formation of PdF$_6^{2-}$ salts.

The crystal structure of Pd(AsF$_6$)$_2$ confirms the presence of highly distorted AsF$_6^-$ anions as predicted by vibrational spectroscopy. It is composed of 2D slabs containing Pd atoms in the center and AsF$_6$ groups on either side. Only van der Waals bonding exists between neighboring slabs. The network can be described as being based on the CdCl$_2$ structural type or the LiSbF$_6$ type (ordered ReO$_3$), with ordered vacancies (□) for half the cationic sites, i.e. Pd$_{0.5}$□$_{0.5}$AsF$_6$. 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 $M^{II}(X^VF_6)_2$ (*M* = transition metal; *X* = As, Sb, Bi, Nb, Ta). Two exceptions are Mn(AsF$_6$)$_2$ [37] and Pd(NbF$_6$)$_2$.[38]

The paramagnetic behavior of Pd(AsF$_6$)$_2$ is in good agreement with the structural data because no Pd−F−Pd superexchange interaction is possible.

## Experimental Section

**Apparatus and Reagents:** Volatile materials (AsF$_5$, PF$_5$, 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 $n(PdF_2):n(AsF_5) = 1:1.87$. $Pd(AsF_6)_2$ (484.2): calcd. Pd 21.97, F 47.09, As 30.94, $AsF_6$ 78.03; found Pd 23.2, F 45.3, As 30.6, $AsF_6$ 76.1 [corresponding to molar ratio $n(PdF_2):n(AsF_5) = 1:1.87$]. In other experiments different final molar ratios $n(PdF_2):n(AsF_5)$ were obtained giving "$PdF_x(AsF_6)_{2-x}$" 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), $AsF_5$ (20.56 mmol) and $F_2$ (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. $Pd(AsF_6)_2$ (484.2): calcd. Pd 21.97, F 47.09, As 30.94, $AsF_6$ 78.03; found Pd 21.4, F 46.1, As 33.8, $AsF_6$ 77.3 [corresponding to molar ratio $n(Pd):n(As):n(AsF_6):n(F) = 1.0:2.2:2.0:12.1$].

**Reaction between Pd and AsF$_5$ in aHF in the Presence of a Large Excess of Fluorine:** Reaction mixture: Pd (0.326 g, 3.06 mmol), $AsF_5$ (25.15 mmol) and $F_2$ (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 $Pd_2F_6$. The XRPD-pattern of green solid isolated from decanted solution showed only $Pd(AsF_6)_2$.

**Reaction between Pd$_2$F$_6$ and H$_2$ in aHF:** $Pd_2F_6$ (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 Pd$^{2+}$ Dissolved in AsF$_5$/aHF:** A clear green blue solution was prepared from Pd (0.133 g, 1.26 mmol), $AsF_5$ (3.700 g, 21.78 mmol) and $F_2$ (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 $Pd_2F_6$.

**Attempted Synthesis of PdFAsF$_6$:** 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 $KPF_6$ (0.266 g, 1.46 mmol) in the other. aHF (about 4 mL), $AsF_5$ (2 g) and $F_2$ (1.60 mmol) were condensed onto the Pd and in the other arm aHF (3 mL) was condensed onto $KPF_6$, 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 $KPF_6$ in aHF was slowly poured onto the clear solution of $Pd(AsF_6)_2$ 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 $PdF_2$.[9] The XRPD-pattern and Raman spectrum of the solid

precipitated from the decanted solution showed a mixture of $KAsF_6$ and $Pd(AsF_6)_2$.

**Preparation of Single-Crystals of Pd(AsF$_6$)$_2$ and Structure Determination:** The crystal structure of $Pd(AsF_6)_2$ 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 $Pd(AsF_6)_2$ was repeated on new crystals. All crystallographic data presented in this paper are from repeated crystal structure determinations.

Single-crystals of $Pd(AsF_6)_2$ were prepared by solvothermal syntheses. The reaction between Pd (0.110 g, 1.03 mmol), $AsF_5$ (1.5 g, 8.83 mmol), aHF (0.050 g) and $F_2$ (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 $Pd(AsF_6)_2$ were found inside. Single-crystals were selected in a drybox and mounted in 0.3 mm quartz capillaries.

Single-crystal data from $Pd(AsF_6)_2$ were collected on a Mercury CCD area detector coupled with a Rigaku AFC7S diffractometer using monochromated Mo$K_\alpha$ 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 $Pd(AsF_6)_2$

| | |
|---|---|
| Formula | $Pd(AsF_6)_2$ |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ (No.2) |
| Unit cell dimensions (pm,°) | $a = 500.9(5)$ |
| | $b = 538.3(5)$ |
| | $c = 864.9(9)$ |
| | $\alpha = 74.46(3)$ |
| | $\beta = 89.97(4)$ |
| | $\gamma = 62.47(2)$ |
| $V$ (nm$^3$) | 0.1972(3) |
| $D_{calcd.}$ (gcm$^{-3}$) | 4.079 |
| $Z$ | 1 |
| Molecular mass (gmol$^{-1}$) | 484.24 |
| Wavelength (pm) | 71.069 |
| Temperature (K) | 293(2) |
| θ range for data collection (°) | $2.47 \leq \theta \leq 29.00$ |
| Index ranges | $-6 \leq h \leq 6, -6 \leq k \leq 6,$ |
| | $-6 \leq l \leq 11$ |
| Reflections collected | 898 |
| Independent reflections | 796 ($R_{int} = 0.0256$) |
| Observed reflections [$I > 2\sigma(I)$] | 762 |
| Refinement method | Full matrix least-squares on $F^2$ |
| Data/restraints/parameters | 796/0/70 |
| Absorption correction | multi-scan |
| Absorption coefficient (mm$^{-1}$) | 10.864 |
| Goodness-of-fit on $F^2$ | 1.061 |
| $R$ indices (all data) | $R1 = 0.0615$, $wR2 = 0.1620$ |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0602$, $wR2 = 0.1599$ |

[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 $Pd(AsF_6)_2$ 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).

## Acknowledgments

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