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Article

On the Existence of Molecular Palladium(VI) Compounds: Palladium Hexafluoride

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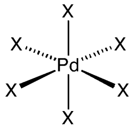
A theoretical study of the accessibility of hexacoordinate palladium(VI) compounds is presented. Species such as $[Pd(SiR_3)_6]$, $[PdCl_6]$, and $[Pd(OH)_6]$ are predicted to be unstable toward reductive elimination of the ligands. In contrast, the presence of a stable palladium(VI) center is expected in $[PdF_6]$, a low-spin nearly octahedral molecule with a weak Jahn–Teller distortion and highly covalent Pd–F bonds. A vibrational analysis confirms such a geometry as an energy minimum, and a special distribution of its spin density makes PdF_6 a highly interesting synthetic target.

Introduction

New trinuclear complexes were synthesized as a product of the thermal condensation of $[Pd(o\text{-}C_6H_4\{SiH_2\}_2)(dpe)]$, where dpe is bis(dialkylphosphino)ethane. The crystal structure shows the metal atom surrounded by six Si atoms,[1] but the unusual $PdSi_6$ fragment has been the object of controversy regarding the assignment of the palladium oxidation state. Thus, the $Pd(SiR_3)_6$ unit was initially formulated as hexasilylpalladium(VI), but the possibility of a palladium(II) oxidation state was suggested as an alternative in an accompanying comment.[2] Following such a proposal, two subsequent papers presented theoretical considerations to conclude that the metal atom must be considered formally as palladium(II).[3,4]

Known and structurally characterized high-valent fluoro complexes of second- and third-row transition metals include MF_6 (M = Mo, W, Re, Os, Ir, and Pt)[5−7] and MF_7 (M = Re and Os),[8] and even PtF_8 has been computationally predicted to be stable.[7] If we focus on group 10 transition metals, PtF_6 was synthesized 50 years ago as a volatile molecule at room temperature[9] and has been structurally well characterized.[6] It has strong oxidizing properties and can liberate F_2[10] or oxidize O_2, forming $O_2^+PtF_6^-$.[11] The preparation of the corresponding palladium fluoride has been reported[12] to proceed by reacting palladium powder with atomic fluorine generated through an electric discharge, although its characterization is based mostly on its IR absorption at the frequency expected for the symmetric stretching mode. It seems clear that $[PdF_6]$ is more difficult to synthesize than $[PtF_6]$, and attempts to electrochemically oxidize salts of the $[PdF_6]^{2-}$ anion have failed, whereas similar methods have been successful for the platinum analogue.[13]

Chart 1



X = SiH_3 (**1**)
Cl (**2**)
NH_2 (**3**)
OH (**4**)
F (**5**)

The goal of this paper is to theoretically investigate the possible existence of palladium(VI) species. In this work, we present a study of hexacoordinate palladium(VI) com-

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plexes, in order to understand the bonding within and clarify their electronic stability. For that purpose, we have initially selected the compounds [Pd(SiH$_3$)$_6$], [Pd(NH$_2$)$_6$], [Pd(OH)$_6$], [PdCl$_6$], and [PdF$_6$] and performed geometry optimizations starting from a pseudooctahedral geometry (Chart 1) for both the low- and high-spin states ($S = 1$ and 2, respectively).

Results and Discussion

Geometry optimization of [PdX$_6$] compounds **1**−**4** in their triplet state shows them to be unstable toward ligand dissociation via reductive elimination, forming X−X bonds and leaving paramagnetic metal fragments with lower coordination numbers. In the former case (**1**), a d^8 palladium(II) square-planar complex [Pd(SiH$_3$)$_2$(η^2-Si$_2$H$_6$)$_2$] results, in which two disilane molecules coordinate through a Si−Si σ bond.[3] These results for the SiH$_3$ ligands agree with the remark made by Crabtree that the isolobal hydrido complex [PdH$_6$][2] generates dihydrogen molecules, as was theoretically predicted and experimentally observed.[14] The same justification has been proposed for the unstable [PtCl$_6$].[15]

In contrast, [PdF$_6$] (**5**) is optimized with a slightly compressed octahedral geometry in its triplet ground state, which is shown by a vibrational analysis to correspond to an energy minimum. The calculated Pd−F$_{eq}$ and Pd−F$_{ax}$ bond distances are 1.894 and 1.890 Å, respectively. These distances are clearly shorter than the mean values found in PdF$_4$ (1.948 Å),[16] PdF$_3$ (2.043 Å),[17] and PdF$_2$ (2.162 Å),[18] all with hexacoordinate Pd atoms and bridging fluoride ligands.[19] The decrease in the bond distance with increasing oxidation state nicely shows the enhanced covalency of the Pd−F bonds (Figure 1). Furthermore, the calculated distances are comparable with the Pt−F bond lengths in PtF$_6$ [1.839(3) and 1.850(5) Å], as determined by extended X-ray absorption fine structure[20] and neutron diffraction[6] methods, respectively. The singlet and quintet states have been found to be 2 and 39 kcal·mol^{-1} higher in energy than the triplet state, respectively, in agreement with the well-known fact that hexafluoro complexes of second- and third-row transition metals present low-spin configurations,[21] including PtF$_6$.[22]

The different behavior of the five studied compounds can be rationalized by the high electronegativity of palladium(VI) compared to silyl, chloride, amide, and hydroxo groups, which makes a ligand-to-metal electron-transfer thermodynamically favored. On the contrary, the most electronegative element, fluorine, can still retain its valence electrons in the presence of palladium(VI). An additional outcome of the high oxidation state of palladium is a strongly covalent character of the Pd−F bonds in PdF$_6$, as will be discussed below.

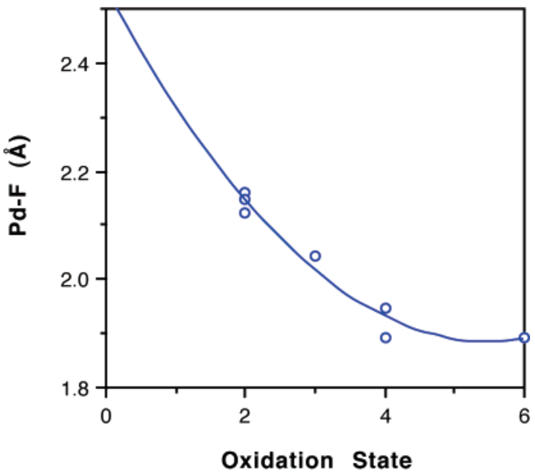

Figure 1. Dependence of the Pd−F bond distance on the oxidation state in compounds with PdF$_6$ octahedral fragments. The value for palladium(VI) corresponds to the average of the calculated Pd−F distance in this work, whereas the rest of the values come from X-ray structural determinations (see the text for references).

Let us briefly discuss the main characteristics of the electronic and molecular structures of [PdF$_6$]. The t$_{2g}$ orbitals are now occupied by only four electrons in the triplet ground state, i.e., $t_{2g}{}^{3\alpha}t_{2g}{}^{1\beta}$, consistent with a formal palladium oxidation state of 6+. The π nature of the interactions involved in the Jahn−Teller effect accounts for both the small differences in the bond lengths (0.004 Å) and a small orbital gap giving rise to the triplet ground state. Recent calculations on the analogous PtF$_6$ showed also a triplet to be the ground state,[7] and the presence of σ,π(F) → t$_{2g}$(Pt) charge-transfer bands, together with the magnetic behavior,[22] indicates that [PtF$_6$] has the same electronic structure as that proposed here for PdF$_6$.

The weak compression of axial bonds in PdF$_6$ is in agreement with the presence of the Jahn−Teller distortion expected for a d^4 complex, resulting in a $(xy)^2(xz)^1(yz)^1$ electron configuration (Figure 2). Our calculations show that such a weak distortion from an ideal octahedron (one with all Pd−F distances at 1.891 Å) stabilizes the molecule by only 0.5 kcal·mol^{-1}, in keeping with the π nature of the t$_{2g}$ orbitals involved. A slight distortion has been found for PtF$_6$ (Pt−F$_{eq}$ = 1.848; Pt−F$_{ax}$ = 1.844 and 1.859 Å) in the solid state,[6] and a recent computational study has shown the distorted geometry in this case to be 4 kcal·mol^{-1} more stable than the ideal octahedral one.[7] Interestingly, the F−Pd−F bond angles show a distortion of T_{2u} symmetry from the octahedron (**6**), with each axial fluorine having two trans equatorial ligands forming angles of 92.2 and 87.8°. Given the noncentrosymmetric nature of such a distortion, it cannot be accounted for by a first- or second-order Jahn−Teller effect involving only the centrosymmetric d orbitals. It can

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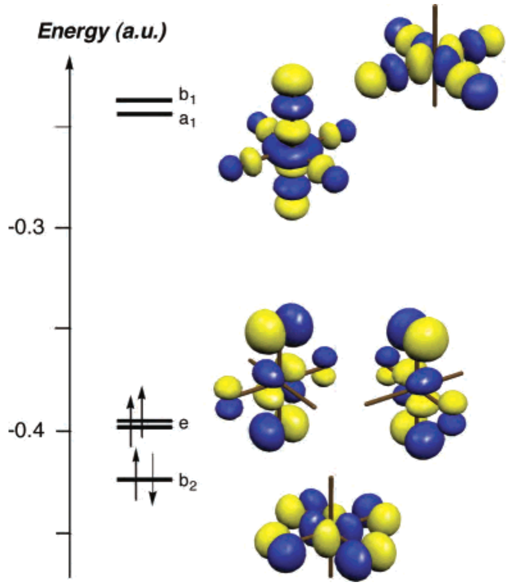


Figure 2. Kohn−Sham frontier orbitals in PdF_6. The orbital energies given are averages for the α and β spin orbitals, whereas the contours shown correspond to the α functions in all cases.

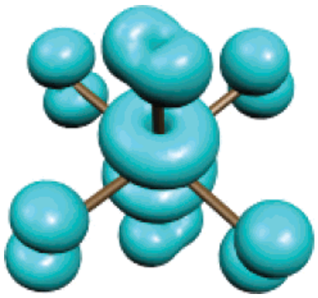
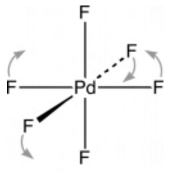


Figure 3. Spin-density distribution calculated for PdF_6 in its triplet ground state. The contour shown corresponds to 0.01 electrons.

rather be ascribed to a decrease in the π-antibonding character of the doubly occupied b_2 orbital.



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The spin-density distribution can be understood in terms of the qualitative molecular orbital theory, backed up by the analysis of the Kohn−Sham orbitals. Although the two unpaired electrons are formally centered at the Pd atom (see a depiction of the corresponding orbitals in Figure 2), the spin density at the Pd atom is only 0.6 electrons, consistent with a strong covalency of the Pd−F bonds, which delocalizes about 0.2 unpaired electrons to each F atom (see Table 1). The shape of the spin-density distribution (Figure 3) is quite unusual[23] and deserves some comment. The cylindrical symmetry of the spin density around the Pd atom and the existence of a nodal plane are the result of the presence of unpaired electrons in both the d_{xz} and d_{yz} metal orbitals. These orbitals delocalize the spin density via covalency of the Pd−F bonds to the p_x and p_y orbitals of the axial F atoms that combine to give the ellipsoidal shapes on those atoms. The equatorial F atoms receive spin density only in their p_z orbitals, resulting in spin densities with the shape of p orbitals. PdF_6 is also an interesting target for the experimental determination of its spin density, although the presence of an orbital contribution to the magnetic moment may complicate the analysis.

Table 1. Atomic and d Orbital Spin Populations (in Electrons) in Fully Optimized PdF_6

	Mulliken	natural population analysis
Pd	+0.65	+0.57
xy	+0.00	−0.01
xz	+0.35	+0.23
yz	+0.35	+0.23
F_{eq}	+0.23	+0.25
F_{ax}	+0.21	+0.22

Table 2. Calculated Vibrational Spectrum for PdF_6 and Comparison with Available Related Data[a]

		PdF_6		PtF_6
mode	symmetry[b]	calcd	estim.[c]	exptl[d]
ν_a	B_2	585 (100)	711	705 (vs)
ν_a	A_1	544	590	656
ν_d	E	530 (8)	711	705 (vs)
ν_s	A_1	505	525	601
ν_d	B_1	503	525	601
δ_d	E	262 (20)	280	273 (vs)
δ_d	E	246 (30)	191	211 (na)
δ_a	B_1	203	191	211 (na)
δ_s	B_2	199 (49)	280	273 (vs)
π	E	171 (31)	255	242
π	A_1	102	255	242

[a] Frequencies in cm^{-1}; IR intensities (in parentheses) in relative units. [b] The assignment corresponds to D_{2d} symmetry.[25] [c] Interpolated from experimental data for metal hexafluoride compounds assuming a regular octahedral geometry.[24] [d] Experimental spectrum for PtF_6 (O_h symmetry; vs, very strong; na, not available).[26]

A vibrational analysis provides us with useful information for the future identification of PdF_6 via IR and Raman spectroscopy. The calculated bands for PdF_6 are presented in Table 2, together with estimates for the IR bands obtained by interpolation from the spectra of the analogous transition-metal fluorides assuming ideal O_h symmetry.[24] There, it can be seen that the IR spectrum is dominated by the asymmetric B_2 stretching mode (corresponding to A_{2u} in the ideal O_h symmetry) predicted at 585 cm^{-1}, while other stretching modes should be observable in the Raman spectrum between 500 and 550 cm^{-1}. Four bands corresponding to bending modes are expected in the IR between 170 and 270 cm^{-1}.

The thermal stability of PdF_6 is also an interesting subject.[12] Thus, as has been observed for PtF_6 at high temperature,[27] one could propose its thermal decomposition to proceed through the following reaction in the gas phase:

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$$PdF_6(g) \rightarrow PdF_4(g) + F_2(g)$$

The most stable structure for PdF_4 has a pseudoplanar geometry (D_{2d} symmetry with F−Pd−F = 167°) having four Pd−F distances at 1.89 Å and a triplet as the ground state (see the Supporting Information). In this case, the spin-allowed reaction is endoergonic by only +0.14 kcal·mol^{-1},[28] but one can expect the formation of solid PdF_4,[16] with diamagnetic hexacoordinated metal centers linked by fluoro bridges as in PtF_4, can displace this equilibrium to the right.[29] Moreover, we notice that molecular PdF_4 presents two intense bands at 592 and 157 cm^{-1}, which could overlap with those of PdF_6 and prevent identification by vibrational spectroscopy in the gas phase.

Conclusions

In summary, we can conclude that, among the molecules of the [PdX_6] type theoretically studied (X = F, OH, NH_2, Cl, and SiH_3), only PdF_6 is expected to be stable in its low-spin state, featuring a Pd atom in a formal oxidation state of 6+. The calculated vibrational spectral data are provided to facilitate future experimental identification of such a special molecule. As expected from its t_{2g}^4 configuration, PdF_6 is paramagnetic and subject to a weak compression of axial bonds due a second-order Jahn−Teller distortion involving π orbitals. In contrast, other hypothetical [PdX_6] compounds are unstable and evolve toward the formation of X−X bonds because of the strong oxidizing power of palladium(VI).

Computational Details

Density functional theory (DFT) calculations were carried out using the *Gaussian98* package.[30] The hybrid DFT method (U)B3LYP was applied, in which the Becke three-parameter exchange functional[31] and the Lee−Yang−Parr correlation functional were used.[32] Basis sets including effective core potentials were used for Pd atoms[33] adding an extra f-polarization function for Pd[34] and using a 6-311++G** basis set for F.[35] Similar results were obtained in preliminary calculations with a low-quality basis set detailed in our previous paper.[3]

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Supporting Information Available: Tables and figures containing atomic coordinates of PdF_6 and optimized parameters, a d orbital energy diagram, vibrational data, and spin densities of PdF_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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