

Notes

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A Neutron Powder Diffraction Study of Palladium Tetrafluoride

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X-ray powder diffraction patterns of the recently synthesized² tetrafluorides of rhodium, iridium, and palladium indicate isomorphism with platinum tetrafluoride. Although the trifluorides, pentafluorides, and hexafluorides of the platinum group metals are in sixfold coordination, early work³ suggested that the tetrafluorides were isostructural with UCl_4 in which the uranium atom is in eightfold coordination. More recently, however, on the basis of an x-ray powder pattern, IrF_4 has been shown to have an orthorhombic space group ($Fdd2$)⁴ in which iridium is six-coordinate. Furthermore, a neutron diffraction study⁵ of the structure of palladium trifluoride shows different environments for the Pd(II) and Pd(IV) atoms, though for each there is sixfold coordination by fluorine. The mean Pd-F bond length for the atom presumed to be Pd(IV) is 1.90 Å compared with a mean Ir-F distance of 1.96 Å in IrF_4 .⁴

We report here the structure of PdF_4 which in the absence of single-crystal specimens is based on a refinement of neutron powder diffraction data using the well-established method of profile analysis.⁶ In the profile refinement technique, an attempt is made to match the detailed shape or profile of the whole pattern using a structural model for which the atomic positions can be varied according to a least-squares procedure. The method is more powerful than conventional powder diffraction methods and can in certain cases be competitive with single-crystal techniques for moderately complex structures.⁷ In addition, the fact that the neutron scattering lengths of Pd and F are similar allows a more accurate determination of the fluorine position than a powder x-ray study.

Diffraction Measurements and Refinement

The PdF_4 powder was prepared by the method of Rao et al.² The compound is highly reactive with air; it was therefore sealed under vacuum into a thin-walled aluminium tube immediately after preparation. The diffraction pattern was obtained on the $D2$ diffractometer at the Institut Laue-Langevin using a neutron beam monochromator to give a wavelength of 1.060 Å. The $D2$ instrument has low resolution but high intensity of the incident beam which enables collection of powder diffraction data in a short time. The 2θ range (8–75°) was covered in 8 h with a counting interval of 0.1° (2θ). A second pattern was obtained using an empty identical aluminium tube in place of the sample. This pattern consisted of weak diffraction peaks and some background intensity and was subtracted to give a profile for the PdF_4 sample alone.

The program for profile analysis minimizes the function

$$\chi^2 = \sum_i W_i |y_i(\text{obsd}) - (1/C)y_i(\text{calcd})|^2$$

where W_i is a weighting factor, y_i the number of counts for a particular value of 2θ , and C the scaling factor.

Table I. Structural and Positional Parameters and Temperature Factors for PdF_4 and IrF_4

	Parameters	PdF_4 (this work)	IrF_4 ³
	<i>a</i>	9.339 (5)	9.64 (1)
	<i>b</i>	9.240 (7)	9.25 (1)
	<i>c</i>	5.828 (3)	5.67 (1)
8 metal atoms in (a)	<i>x</i>	0	0
	<i>y</i>	0	0
	<i>z</i>	-0.005 (0.012)	-0.04
	<i>B</i> , Å ²	0.55 (0.13)	
16 bridging fluorine atoms in (b)	<i>x</i>	0.157 (0.001)	0.15
	<i>y</i>	0.132 (0.001)	0.13
	<i>z</i>	0	0
	<i>B</i> , Å ²	0.65 (0.05)	
16 nonbridging fluorine atoms in (b)	<i>x</i>	0.158 (0.001)	0.17
	<i>y</i>	0.141 (0.001)	0.14
	<i>z</i>	0.489 (0.002)	0.50
	<i>B</i> , Å ²	0.65 (0.05)	

A profile residual based on the weighted intensities of the profile at each point is defined as

$$R(\text{weighted profile}) = 100 \left[\frac{\sum_i W_i |y_i(\text{obsd}) - (1/C)y_i(\text{calcd})|^2}{\sum_i W_i |y_i(\text{obsd})|^2} \right]^{1/2}$$

The starting model for the refinement was the idealized structure suggested by Rao et al.² based on space group $Fdd2$ (see Table I) with eight molecular units per cell.

Independent isotropic Debye-Waller factors for Pd and F, six variable atomic coordinates and the three lattice parameters, were simultaneously refined using values of $b_{Pd} = 0.60 \times 10^{-12}$ cm and $b_F = 0.560 \times 10^{-12}$ cm⁸ for the scattering lengths of palladium and fluorine, respectively. Three parameters required to define the resolution function of the instrument were also allowed to vary. The refinement converged after five cycles to give atomic coordinates similar to those obtained for IrF_4 in the x-ray study (see Table I). The value of $R(\text{weighted profile})$ is 14.1% which is higher than expected from the statistics of the counts. In the present case, however, additional uncertainty is introduced because of the need to subtract the profile of the empty aluminium tube. Figure 1 shows the calculated and observed profiles together with a difference curve. A profile fit based on the atomic coordinates of IrF_4 gives a high $R(\text{weighted profile})$ of 23.3%, but the relatively low precision of the IrF_4 determination does not enable us to state whether there is a significant difference between the two structures.

In the present study the positional parameters are precisely determined (to better than 0.002 in *x*, *y*, *z* coordinates) except for the *z* coordinate of palladium. The reason for the lower precision of this parameter is not clear. It may be due in part to the small number of reflections in the pattern for which *l* is dominant, which arises from the short *c* axis and frequent extinction of *Ok**l* and *h*0*l* reflections.

Discussion

The present results taken with those of IrF_4 confirm octahedral coordination of the tetrafluorides of the platinum groups. The fluorine ligands are not all equivalent, in that four are bridging atoms and two are terminal atoms arranged in a cis configuration (see Figure 2). Despite this asymmetry

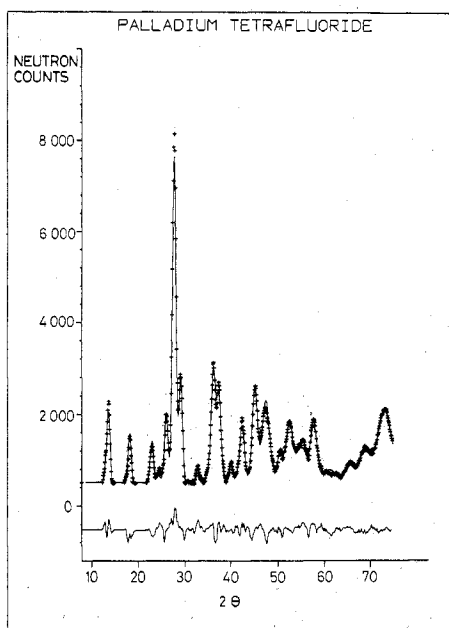


Figure 1. Powder pattern for PdF₄ obtained on the D2 diffractometer (λ 1.060 Å): +, observed intensities; -, calculated intensities. The difference curve is shown below.

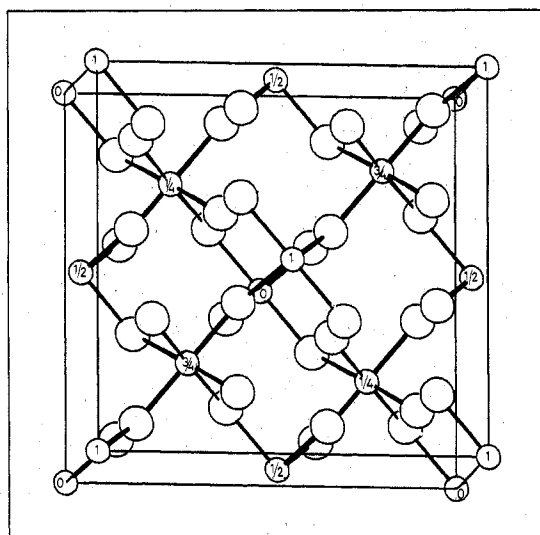


Figure 2. Unit cell of PdF₄ projected on the *a-b* plane (viewed obliquely): Pd, small circles marked with the fractional *z* coordinate along *c*; F, large circles.

Table II. Bond Lengths (Å) and Angles (deg) for PdF₄ and IrF₄

Bond Lengths			
Pd-F(bridging)	1.91 (1),	Ir-F(bridging)	1.90,
	2.00 (5)		1.89
Pd-F(nonbridging)	1.94 (5)	Ir-F(nonbridging)	2.08
Bond Angles			
Ir-F-Ir (bridge)	147		
Pd-F-Pd (bridge)	134.0 (2.4)		
F(bridging)-Pd-F(bridging)	91.4 (1.5), 89.8 (1.5), 89.8 (1.5),		
F(bridging)-Pd-F(nonbridging)	91.5 (1.5), 88.6 (2.8),		
F(bridging)-Pd-F(terminal)	88.8 (1.5), 89.8 (1.6), 89.8 (1.6),		
F(terminal)-Pd-F(terminal)	88.9 (1.6), 92.7 (0.4), 92.7 (0.4)		
F(terminal)-Pd-F(terminal)	85.9 (2.8)		

the PdF₆ octahedra are approximately regular. The differences observed in bond lengths and bond angles within the PdF₆ octahedron are generally less than twice the calculated errors (see Table II). In addition, the observed Pd-F-Pd bridging

angle of $134 \pm 2.4^\circ$ agrees well with that required (135°) for ideal hexagonal close packing of octahedra. We are not therefore able to distinguish between the Pd-F(bridging) bond lengths and the Pd-F(nonbridging) distances although we might expect the nonbridging bond to be shorter. In AuF₃⁹ for example the fluorine bridges have a bond length of 2.04 Å compared to 1.91 Å for the terminal fluorine ligands, although in this low-spin d⁸ compound there is a gross distortion of the AuF₆ octahedra toward square planar leaving two longer Au-F distances at 2.69 Å.

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Registry No. PdF₄, 13709-55-2.

References and Notes

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Tetrachlorophosphonium Oxotetrachlorochromate(V)

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The reaction between chromium(VI) dioxide dichloride and phosphorus pentachloride has been reported several times this century.¹⁻⁵ At high temperature^{4,6} or in the presence of a reducing agent,^{2,3,5} the product has been identified as tetrachlorophosphonium tetrachlorochromate(III), (PCl₄)[CrCl₄]. At room temperature,^{1,3} the product was described as an adduct of chromium(VI) dioxide dichloride, CrO₂Cl₂·PCl₅. As part of our investigations into the chemistry of chromium(V),^{7,8} we have reinvestigated this system, as the formation of a chromium(VI) adduct did not appear to be in accord with chemical experience (reports of the existence of CrO₂Cl₂(py),⁹ CrO₂Cl₂(py)₂,⁹ and CrO₂Cl₂(bpy)¹⁰ (py = pyridine; bpy = 2,2'-bipyridine) have recently been shown to be erroneous¹¹). We find that the product of the reaction between CrO₂Cl₂ and PCl₅, at room temperature, in both polar and nonpolar solvents, is the novel complex tetrachlorophosphonium oxotetrachlorochromate(V), (PCl₄)[CrOCl₄], and report some of its spectroscopic properties. We also discuss the nature of (PCl₄)[CrCl₄].

Results and Discussion

The reaction between chromium(VI) dioxide dichloride and phosphorus pentachloride, in both phosphorus oxide trichloride and carbon tetrachloride, yields a solid (red-brown microcrystals or orange-brown powder, respectively) of empirical formula Cl₈CrOP, and not Cl₇CrO₂P as previously reported.^{1,3} The products from both solvents had similar infrared and electronic spectra, were extremely air sensitive, and were