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The crystal structure of palladium difluoride.

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Introduction

Palladium difluoride, contaminated with metal, was first prepared by Ruff & Ascher (1929), who characterized the compound by its X-ray powder pattern, which indicated that it forms tetragonal crystals of the rutile type. Ebert (1931) confirmed the earlier work and gave unit-cell dimensions but did not complete the structure determination. The recent development in these laboratories of a method for the preparation of pure palladous fluoride has provided samples suitable for such a structure determination (Bartlett & Hepworth, 1956).

Experimental

PdF_2 was prepared by the reduction of palladic fluoride with selenium tetrafluoride and the sample was heated in the tetrafluoride vapour at 280 °C. for 30 minutes. This temperature is somewhat higher than that used for the preparation of pure samples of the difluoride (which were unfortunately poorly crystalline) and the resulting material contained a small quantity of palladium metal. Since palladous fluoride is hydrolysed in moist air, thin walled X-ray specimen capillaries, 0·5 mm. diameter (supplied by Pantak Ltd, Slough) were filled and sealed off in a dry box.

X-ray powder photographs were taken at 18±2 °C. in a 19 cm. Unicam camera, using crystal-reflected Fe$K\alpha$ radiation ($\alpha_1\lambda = 1{\cdot}93597$; $\alpha_2\lambda = 1{\cdot}93991$ Å) from a lithium–fluoride monochromator. Duplicate films, which showed low background intensities, were microphotometred with a Dobson-type instrument built from a design by Taylor (1951), and values of the integrated intensities in arbitrary units were obtained by measuring areas under the plotted photometer curves with a planimeter. For any line in a powder photograph, the intensity is given by

$$I = \text{constant } F^2_{hkl}(1+\cos^2 2\alpha \cos^2 2\theta)/(\sin^2\theta \cos\theta) \times \text{p.A.} \exp\left[-B(\sin\theta/\lambda)^2\right]$$

where α is the angle of reflexion in the monochromator, and other symbols have their usual meanings. In calculating intensities Hönl's absorption-edge effect was taken into account (James, 1948, pp. 160, 608); the absorption and an arbitrary temperature factor were obtained by standard methods.

Results

All observed X-ray reflexions, were with the exception of the faint lines of palladium metal, indexed on a tetragonal cell of the rutile type. Since only one of the palladium reflexions overlapped with a difluoride reflexion the presence of metal did not interfere with the structure determination. The dimensions of the bimolecular unit cell are compared below with those given by Ebert.

a (Å)	*b* (Å)	*c*/*a*	
4·956±0·002	3·389±0·002	0·684	Present work
4·93	3·38	0·687	Ebert

Lack of sharpness in the resolution of the reflexions at high Bragg angles prevented the determination of the cell dimensions with greater accuracy. By trial and error methods, excellent agreement between the observed and calculated intensities (see Table 1) was obtained by placing the atoms in the following positions of space group D^{14}_{4h}–$P4_2/mnm$. (*International Tables for X-ray Crystallography*, 1952, No. 136):

2 Pd atoms at $0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.
4 F atoms at $\pm(u, u, u)$; $\pm(u+\frac{1}{2}, u-\frac{1}{2}, \frac{1}{2})$.

Value of $u = 0{\cdot}310 \pm 0{\cdot}003$.

Table 1. *Calculated and observed X-ray data for* PdF_2 (Fe $K\alpha$ *radiation*)

	Sin² θ		Relative intensities		
hkl	Calc.	Obs.	Calc.		Obs.
110	0 0764	0·0773	99		100
101	0·1199	0·1211	107		109
200	0·1528	0·1540	34	47	46
111	0·1581	0·1591	13		
210	0·1910	0·1915	5		5
211	0·2727	0·2741	228		230
220	0·3056	0 3066	63		63
002	0·3268	0·3283	39		38
310	0·3820	0·3830	65		72
221	0·3873	—	2		—
112	0·4032	0·4045	87		86
301	0·4255	0·4268	129		124
311	0·4637	—	2		—
202	0·4796	0·4807	46		42
320	0·4966	—	6		—
212	0·5178	0·5188	5		*vw*
321	0·5783	0·5790	98		96
400	0·6112	0·6120	39		36
222	0·6324	0·6331	92		95
410	0·6494	0·6507	5		*vvw*
330	0·6876	0·6873	61		61
312	0·7088	0·7088	139		146
411	0·7311	0·7310	171		173
420	0·7640	0·7639	90	168	171
331	0·7693	—	2		
103	0·7735	0·7743	76		
113	0·8117	0·8126	6		*vvw*
322	0·8234	—	1		—
421	0·8457	0·8451	8		*vvw*
213	0·9263	0·9257	385	577	553
402	0·9380	0·9372	191		

Discussion

PdF_2 is isostructural with MnF_2, FeF_2, CoF_2, NiF_2 and ZnF_2. Each palladium atom has six fluorine atoms forming an almost regular octahedron around it. The PdF_6 coordination octahedra are joined by sharing corners. The interatomic distances are given in Table 2.

It is of interest that the compound is the only known paramagnetic compound of divalent palladium and has an effective magnetic moment of 1·84 μ_B at room tem-

Table 2. *Interatomic distances in* PdF_2

4 Pd–F	2·155 Å
2 Pd–F	2·171
8 F–F	3·060
2 F–F	2·664
2 F–F	3·389

perature. The spin-only value for two unpaired electrons is 2·83 μ_B. Since iron, cobalt and nickel difluorides are antiferromagnetic it is probable that the low value of the magnetic moment may arise from antiferromagnetic effects.

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References

BARTLETT, N. & HEPWORTH, M. A. (1956). *Chem. and Ind.* 1425.

EBERT, F. (1931). *Z. anorg. Chem.* **196**, 395.

JAMES, R. W. (1948). *The Optical Principles of the Diffraction of X-rays.* London: Bell.

RUFF, O. & ASCHER, E. (1929). *Z. anorg. Chem.* **183**, 193.

TAYLOR, A. (1951). *J. Sci. Instrum.* **28**, 200.

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Crystal and molecular structure of meso-erythritol.

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From an X-ray crystal analysis of meso-erythritol,

$$CH_2OH.C^*HOH.C^*HOH.CH_2OH$$

which has 'asymmetric' carbon atoms (indicated by asterisks), interesting features of the structure were found.

The space group, C_{4h}^6–$I4_1/a$, previously assigned to meso-erythritol was confirmed (Burgers, 1926; Schoenfeldt, Hermann & Hassel, 1926). A redetermination of the unit-cell dimensions gave the following values

$$a = 12{\cdot}81 \pm 0{\cdot}03, \quad c = 6{\cdot}81 \pm 0{\cdot}02 \text{ Å}\,.$$

There are eight molecules in the unit cell. In accordance with the conclusions given by Burgers (1926), and Schoenfeldt, Hermann & Hassel (1926), each molecule is found to be situated at the centre of symmetry.

An approximate electron-density projection on (001) was obtained with the aid of inequality and image-seeking methods applied to ($hk0$) spectra. The approximate x and y parameters of the atoms were then successively refined by the syntheses of electron-density and difference electron-density. Using the x and y values for each atom obtained from the refined electron-density projection on (001), an effort was made to conform to a plausible molecular structure in the crystal so as to give an approximate value of z for each atom. Refinement of z parameters was done in the same way as x and y parameters. The electron density projected on (001) is shown in Fig. 1, and the structure is illustrated in Fig. 2. R factors are, at the present stage of refinement, 19·8 and 14·6% respectively for ($hk0$) and ($h0l$) spectra with an isotropic temperature factor $B = 2{\cdot}2$ Å^2.

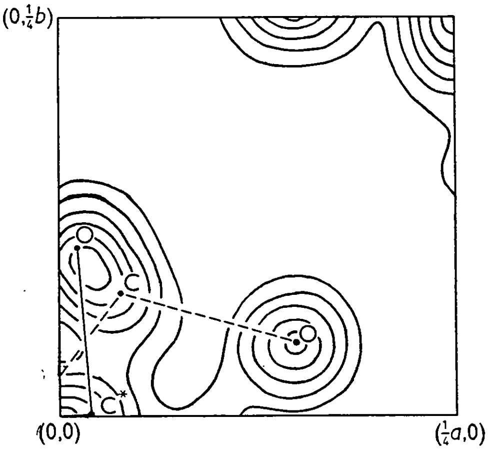

Fig. 1. The (001) electron-density projection; contours at arbitrary intervals.

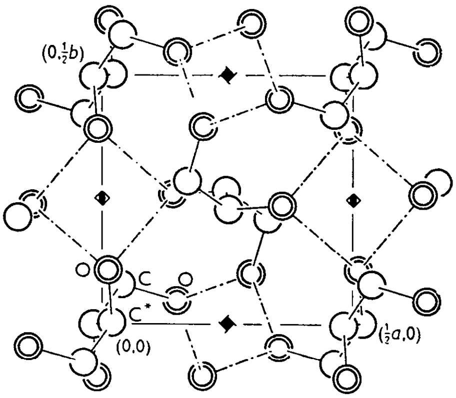

Fig. 2. The structure of meso-erythritol projected on (001), showing the hydrogen bonds by dot-dash lines. Single circles indicate carbon, and double circles oxygen atoms.

Bond distances for the outer and inner carbon–carbon bonds, C*–C and C*–C*, were computed to be 1·54 and 1·55 Å, and those for the outer and inner carbon–oxygen bonds, C–O and C*–O, to be 1·47 and 1·46 Å.