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The Crystal Structure of Palladium Diphosphide

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PdP_2 is monoclinic with four molecules in a cell of dimensions $a = 6{\cdot}207$, $b = 5{\cdot}857$, $c = 5{\cdot}874$ Å; $\beta = 111{\cdot}80°$. The space group is $I2/a$. The Pd atoms are in positions $\pm(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})$, the P atoms in general positions $\pm(xyz)(x, \bar{y}, \frac{1}{2}+z)$ with $x = 0{\cdot}1886$, $y = 0{\cdot}1237$, $z = 0{\cdot}3537$.

A palladium atom forms four square bonds to phosphorus with Pd–P = 2·335 Å and 2·341 Å. The phosphorus atoms are bonded together to form endless zigzag chains with P–P = 2·201 Å and 2·224 Å and a bond angle of 102·0°.

The phases Pd_3P, α-Pd_7P_3, β-Pd_7P_3 and PdP_2 have been observed in the Pd–P system (Raub, Zachariasen, Geballe & Matthias, 1963). The former three of these are superconducting compounds while PdP_2 has other physical properties of interest.

This paper reports the results of a complete structure determination for PdP_2.

Crystals of PdP_2 are monoclinic body-centered with four molecules in a cell of dimensions

$$a = 6{\cdot}207 \pm 0{\cdot}001,\ b = 5{\cdot}857 \pm 0{\cdot}001,$$
$$c = 5{\cdot}874 \pm 0{\cdot}001\ \text{Å};\ \beta = 111{\cdot}80 \pm 0{\cdot}01°.$$

The calculated density is 5·631 g.cm^{-3}. All reflections $(H0L)$ with odd H and L are missing. Thus the suggested space group is $I2/a$ or the subgroup Ia.

Cell dimensions for PdP_2 (in agreement with those given above) have been reported previously by Rundquist (1961), who used a base-centered translation group. Rundquist gave no additional conclusions as to the actual structure, but stated that RhP_2, IrP_2 and NiP_2 are isostructural with PdP_2.

Determination of the structure

Single-crystal fragments were isolated from some of the PdP_2 preparations and ground into small, nearly perfect spheres. The intensity measurements were made on a diffractometer with a proportional counter and Cu $K\alpha$ radiation. A sphere of radius $0{\cdot}0115 \pm 0{\cdot}006$ cm was used to measure all reflections $(HK0)$ and

Table 1. *Structure factors*

HKL	F_o	$0{\cdot}985F_c$	HKL	F_o	$1{\cdot}015F_c$	HKL	F_o	$1{\cdot}015F_c$	HKL	F_o	$0{\cdot}974F_c$
110	28	26	121	24	20	361	21	−21	242	48	47
020	139	−147	211	84	−84	$72\bar{1}$	8	9	$52\bar{3}$	38	35
200	196	−208	031	157	−170	071	55	−49	341	3	1
220	137	130	$32\bar{1}$	73	−66	631	67	70	$51\bar{4}$	38	−36
130	20	−18	$23\bar{1}$	132	−129	$27\bar{1}$	69	−68	143	3	−2
310	49	−45	$41\bar{1}$	141	−142				$32\bar{5}$	49	48
040	52	50	231	166	160			$0{\cdot}974F_c$	$41\bar{5}$	81	−86
400	116	112	321	33	30	110	30	26	$53\bar{2}$	4	−3
330	41	37	$14\bar{1}$	0	2	011	108	105	440	87	85
240	68	−62	141	0	1	$21\bar{1}$	146	135	$23\bar{5}$	62	−63
420	108	−103	411	78	78	$11\bar{2}$	62	−57	044	116	126
150	17	−15	$43\bar{1}$	81	78	$20\bar{2}$	91	101	$54\bar{1}$	0	1
510	40	35	$34\bar{1}$	0	−2	121	21	19	$62\bar{4}$	81	79
440	90	86	051	125	128	220	134	129	$14\bar{5}$	1	−1
350	36	33	$52\bar{1}$	34	29	022	126	128	$63\bar{3}$	69	64
530	33	−31	$25\bar{1}$	102	100	$31\bar{2}$	33	30	$42\bar{6}$	73	77
060	86	−86	341	0	1	$21\bar{3}$	154	−165	$61\bar{5}$	55	54
600	53	−51	431	118	−118	$32\bar{1}$	83	−63	352	4	5
260	81	82	251	124	−126	$12\bar{3}$	50	−46	$51\bar{6}$	14	13
620	81	80	$61\bar{1}$	122	123	231	148	154	253	85	87
170	13	10	521	50	−48	132	47	−33	$33\bar{6}$	28	28
550	32	−28	$16\bar{1}$	44	−42	$41\bar{3}$	135	145	451	93	93
710	14	−12	$54\bar{1}$	0	1	330	42	37	$64\bar{2}$	109	110
460	74	−71	161	14	−13	$42\bar{2}$	123	106	154	25	25
640	96	−98	$45\bar{1}$	66	−65	$31\bar{4}$	24	24	$60\bar{6}$	109	113
			$63\bar{1}$	50	−48	033	89	88	550	32	−28
		$1{\cdot}015F_c$	$36\bar{1}$	45	44	$22\bar{4}$	104	104	$24\bar{6}$	72	72
011	109	109	611	79	−82	$40\bar{4}$	63	70	055	43	43
$21\bar{1}$	141	140	451	96	97	$43\bar{1}$	85	75	$72\bar{5}$	12	12
$12\bar{1}$	78	71	541	0	−1	$13\bar{4}$	7	−6	$73\bar{4}$	22	−22

($HK1$). All reflections (HKL) for which $H+K+L=0$ were measured with a second sphere of radius $0·0257 \pm 0·0010$ cm. The absorption corrections were exceptionally large ($\mu = 888$ cm^{-1}).

Because of the simplicity of the structure, it was an easy task to deduce the approximate atomic positions. The coordinates obtained on the basis of symmetry Ia were found to agree within experimental error with those of the higher space group $I2/a$.

Least-square refinements, with the Busing–Levi IBM 704 program, gave $R = 0·051$ and the following results:

Space group: $I2/a$

Atomic positions: $(000)(\frac{1}{2}\frac{1}{2}\frac{1}{2})+$

$4\text{Pd in } \pm(\frac{1}{4}\frac{3}{4}\frac{1}{4}),\ 8\text{P in } \pm(xyz)(x, \bar{y}, \frac{1}{2}+z)$

$x = 0·1886 \pm 0·0009,\ y = 0·1237 \pm 0·0009,$

$z = 0·3537 \pm 0·0014,$

$B_{\text{Pd}} = 0·322 \pm 0·057$ Å^2, $B_{\text{P}} = 0·162 \pm 0·099$ Å^2.

The agreement between observed and calculated structure factors is shown in Table 1.

Description of the structure

Each palladium atom is bonded to four phosphorus atoms, each phosphorus atom to two palladium atoms and to two phosphorus atoms. The bond lengths, accurate to 0·010 Å or better, are:

Pd–2P = 2·335 Å	P–1P = 2·201 Å
Pd–2P = 2·341 Å	P–1P = 2·224 Å

The observed bond angles are:

P–Pd–P = 88·9° and 91·1°
P–P–P = 102·0°
Pd–P–Pd = 125·0°
Pd–P–P = 95·7°, 107·3°, 110·9°, 111·9°

The phosphorus atoms are bonded together so as to form endless zigzag chains along the a axis. In Fig. 1 these chains are viewed from a direction normal to the chain axis, while Fig. 2 looks at the chains along the chain axis. The chain axes are about 4·0 Å apart and form a nearly square array.

A palladium atom is bonded to four phosphorus atoms, one from each of four phosphorus chains. The five atoms of a PdP_4 configuration lie in a plane, the four phosphorus atoms forming a nearly perfect square about palladium with edges of 3·275 Å and 3·338 Å. As demonstrated in Fig. 2 the PdP_4 groups share corners so as to produce endless, puckered sheets parallel to the (100) plane, held together by P–P bonds between the layers. It is also shown in Fig. 2 that the fundamental unit of a sheet is a pentagon, four edges of which are Pd–P bonds and the fifth a P–P bond. The shortest Pd–Pd distances of 3·104 Å occur between layers, but are so large that little or no binding is indicated.

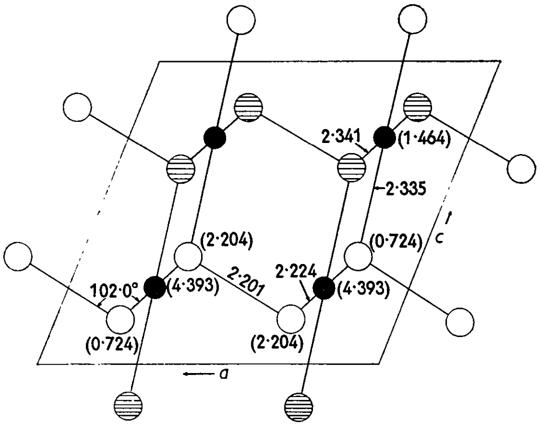

Fig. 1. Structure projected on the (010) plane. Small filled circles represent palladium, large circles phosphorus atoms. Numbers in parentheses give the height in Å above the plane $y = 0$, and numbers on the bonds give their lengths in Å. The open circles represent phosphorus atoms of chains whose axis is at height $b/4$, the hatched circles phosphorus atoms of chains at height $3b/4$.

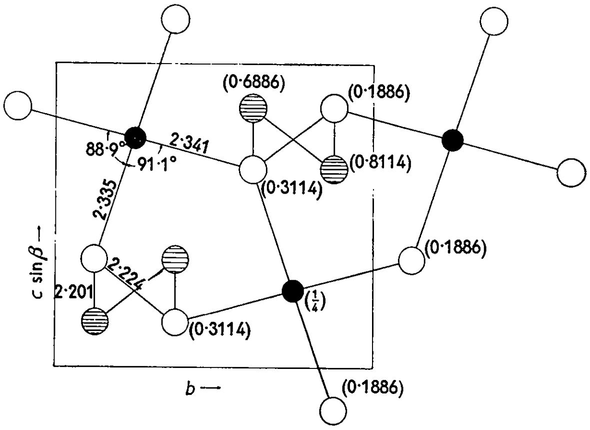

Fig. 2. Structure viewed along the a axis. The projection plane is tilted 21·80° with respect to the plane of the paper, and numbers in parentheses give the x coordinates relative to the projection plane. The hatched circles indicate phosphorus atoms associated with adjacent PdP_2 layers.

The observed bond configurations correspond to Pd^{2-} ($4d5s5p^2$) and P^+ ($3s3p^3$), the hybridization of the four available orbitals giving square bonds for Pd^{2-} and tetrahedral bonds for P^+.

The formation of four square bonds of the dsp^2 hybridization type has been observed previously in a number of compounds of Ni, Pd, Pt, Cu, Ag, and has been discussed in detail by Pauling (1960).

The observed bond distances in PdP_2 give 1·106 Å for the tetrahedral covalent radius of phosphorus and 1·232 Å for the square covalent radius of palladium. The latter value is notably shorter than the 1·32 Å assumed by Pauling.

The samples of PdP_2, from which the single-crystal

fragments were isolated, were prepared by Dr C. J. Raub. One of the two crystal spheres was ground by Miss H. A. Plettinger. The least-square refinement was carried out on the IBM 704 computer of the Argonne National Laboratory. The work was in part supported by the Advanced Research Projects Agency.

The investigation reported in this paper was begun during a visit to the University of California at San Diego. The writer thanks Prof. B. T. Matthias and other La Jolla friends for valuable discussions in a hospitable milieu.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

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The crystal structure of KI.Hg(CN)$_2$. A correction.

By F. H. Kruse, *Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.*

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The paper of the above title (Kruse, 1963) contains an error in Table 4 — *Final observed and calculated structure factors for* KI.Hg(CN)$_2$.

The F_o values for reflections 001, 003, 005, and 009 should be marked with a minus sign denoting 'less than' for these unobserved values, thus making the data table compatible with the space group, *Cmcm.*

Reference

Kruse, F. H. (1963). *Acta Cryst.* **16**, 105.

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Treatment of anomalous dispersion in X-ray diffraction data.

By A. L. Patterson, *The Institute for Cancer Research, Fox Chase, Philadelphia* 11, *Pennsylvania, U.S.A.*

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The purpose of this note is to reemphasize and to amplify the remarks made by Templeton (1955) concerning the importance of the correction of X-ray data for anomalous dispersion effects in the refinement of crystal structures. We are not concerned here with the important uses of such data in the initial approach to the solution of the phase problem.

First, let us assume that there is only one element in the crystal which shows appreciable dispersive effects. This element may be located in one or more sets of general or special positions and is assumed to have structure factor components $A_d=f_dH_d$ and $B_d=f_dK_d$ where f_d is the non-dispersive part of the scattering factor for the dispersive atom at rest and the geometrical components H_d and K_d are assumed to contain isotropic or anisotropic temperature factors appropriate for the thermal motion of the atoms of the dispersive element in the crystal. The structure factor components for the non-dispersive part of the crystal are taken as A_n and B_n. We define F_+ as the structure factor for the plane hkl for which A_n, B_n, A_d, B_d are calculated. Then F_- is that for the plane $\bar{h}\bar{k}\bar{l}$ the inverse of the first. The structure factors for these two planes may then be written in the well known form (*cf.* James, 1948)

$$F_{\pm}=A_n+i\sigma B_n+(H_d+i\sigma K_d)(f_d+\Delta f'_d+i\Delta f''_d)\,, \qquad (1)$$

in which $\sigma=+1$ corresponds to F_+, $\sigma=-1$ corresponds to F_-, and $\Delta f'_d$ and $\Delta f''_d$ are the real and imaginary components of the dispersive effect for the given atom. The result (1) may then be rewritten in the forms

$$\begin{aligned}F_{\pm}&=A_n+i\sigma B_n+(A_d+i\sigma B_d)(1+\delta_1+i\delta_2)\\&=(A+\delta_1A_d-\sigma\delta_2B_d)+i\sigma(B+\delta_1B_d+\sigma\delta_2A_d)\,, \qquad (2)\end{aligned}$$

where A and B are the non-dispersive structure factor components for the whole structure, and

$$\delta_1=\Delta f'_d/f_d\,; \qquad (2a)$$

$$\delta_2=\Delta f''_d/f_d\,. \qquad (2b)$$

We now calculate

$$\begin{aligned}|F_{\pm}|^2=A^2+B^2+(\delta_1^2+\delta_2^2)(A_d^2+B_d^2)+2\delta_1(AA_d+BB_d)\\-2\sigma\delta_2(AB_d-BA_d) \qquad (3)\end{aligned}$$

and define the quantities S and D as

$$\begin{aligned}S=\tfrac{1}{2}\{|F_+|^2+|F_-|^2\}=A^2+B^2+2\delta_1(AA_d+BB_d)\\+(\delta_1^2+\delta_2^2)(A_d^2+B_d^2) \qquad (4a)\end{aligned}$$

and

$$D=\tfrac{1}{2}\{|F_+|^2-|F_-|^2\}=-2\delta_2(AB_d-BA_d)\,. \qquad (4b)$$

One could of course make use of formula (3) to calculate