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Palladium Metaborate

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Abstract. PdB_2O_4, tetragonal, $I\bar{4}2d$, $a = 11\cdot672$ (2), $c = 5\cdot698$ (1) Å, $V = 776$ (1) Å^3, $Z = 12$, $M_r = 192\cdot02$, $D_c = 4\cdot92$ Mg m^{-3}, μ(Mo $K\alpha$) = $2\cdot117$ mm^{-1}. 476 non-equivalent reflections with $I > 3\sigma(I)$ were measured up to sin $\theta/\lambda = 0\cdot66$ Å^{-1}; $R(F) = 0\cdot020$. The structure is isotypical with its Cu analogue. The average Pd–O bond distance is $2\cdot033$ (5) Å.

Introduction. By applying hydrostatic pressure of about 40×10^8 Pa to a 1:1 mixture of $Pd(NO_3)_2.2H_2O$ and B_2O_3 at 1073 K for 6 h followed by rapid quenching the first borate of palladium was obtained in the form of idiomorphic, dark-brown to black crystals of up to 500 μm. The crystal form is a combination of the predominant tetragonal scalenohedron and the tetragonal prisms {100}. The morphological aspect of the crystals is that of a tetrahedron. Preliminary investigations showed the strong relationship between this new compound and the already known CuB_2O_4 (Martínez-Ripoll, Martínez-Carrera & García-Blanco, 1971). In a preliminary report this relationship was stated and interplanar distances were given (Depmeier, Schmid & Haenssler, 1980). Lattice parameters obtained from powder work and given in that report agree very well with the single-crystal results given here. The latter have been obtained from a least-squares refinement of the 2θ values of 54 reflections situated between 7·959 and 54·983° and centred on a Philips PW 1100 diffractometer with Zr-filtered Mo $K\alpha$ radiation. This was also used for the data collection with a crystal of the form of a tetrahedron with edge lengths of about 0·25 mm. Four equivalent reflections were measured up to sin $\theta/\lambda = 0\cdot66$ Å^{-1}, yielding a total of 1994 reflections. Two test reflections measured after every 100 min showed no significant change during the data collection. The equivalent reflections were averaged, resulting in 478 non-equivalent reflections, 476 of which with $I > 3\sigma(I)$ were classed as observed and were used for the refinement. No absorption correction was applied ($\mu R \sim 0\cdot4$). The atomic positions of CuB_2O_4 (Martínez-Ripoll, Martínez-Carrera & García-Blanco, 1971) were used as a starting point and this model refined immediately. The occurrence of negative temperature-factor coefficients was overcome by performing an isotropic-extinction correction. The final R value was $R(F) = 0\cdot020$ with anisotropic temperature-factor coefficients for Pd and O, but isotropic temperature factors for B. All calculations were carried out with the XRAY system (1976) on the Univac 1100 computer of the University of Geneva. Table 1 lists the final atomic positions and Table 2 the bond lengths and angles.*

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36356 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* $(\times 10^4)$ *and equivalent Debye–Waller factors* $(\times 10^3)$ (*isotropic U for boron*)

	Wyckoff notation	Point symmetry	x	y	z	U_{eq}/U (Å^2)
Pd(1)	4(b)	$\bar{4}$	0	0	5000	3·1 (2)
Pd(2)	8(d)	2	802 (1)	2500	1250	3·1 (2)
O(1)	16(e)	1	1619 (3)	702 (3)	4978 (7)	3 (1)
O(2)	8(d)	2	2498 (5)	2500	6250	3 (1)
O(3)	8(d)	2	2500 (4)	893 (5)	8750	6 (1)
O(4)	16(e)	1	737 (3)	1878 (3)	7922 (6)	3 (1)
B(1)	16(e)	1	1843 (5)	1490 (5)	6979 (10)	5 (1)
B(2)	8(d)	2	·8 (7)	2500	6250	1 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

Coordination of Pd(1)		Coordination of Pd(2)	
4× Pd(1)—O(1)	2·060 (4)	2× Pd(2)—O(4)	2·032 (4)
		Pd(2)—O(3)	1·980 (6)
		Pd(2)—O(2)	1·983 (6)
O(1)—Pd(1)—O(1)′	90·0 (1)	O(3)—Pd(2)—O(4)	87·9 (1)
O(1)—Pd(1)—O(1)″	179·3 (2)	O(3)—Pd(2)—O(2)	180·0 (1)
		O(2)—Pd(2)—O(4)	92·1 (1)
		O(4)—Pd(2)—O(4)′	175·7 (2)
B(1) tetrahedron		B(2) tetrahedron	
B(1)—O(1)	1·488 (7)	2× B(2)—O(1)	1·484 (6)
B(1)—O(2)	1·465 (7)	2× B(2)—O(4)	1·480 (6)
B(1)—O(3)	1·446 (7)		
B(1)—O(4)	1·469 (7)		
O(1)—B(1)—O(2)	111·8 (4)	O(4)—B(2)—O(1)	106·5 (2)
O(1)—B(1)—O(4)	108·5 (4)	O(4)—B(2)—O(4)′	108·0 (6)
O(1)—B(1)—O(3)	109·3 (5)	O(4)—B(2)—O(1)′	110·9 (2)
O(2)—B(1)—O(4)	108·3 (5)	O(1)—B(2)—O(4)′	110·9 (2)
O(2)—B(1)—O(3)	108·0 (5)	O(1)—B(2)—O(1)′	113·8 (6)
O(3)—B(1)—O(4)	111·0 (4)	O(4)′—B(2)—O(1)′	106·5 (2)

Discussion. This new compound is isotypical with CuB_2O_4 (Martínez-Ripoll, Martínez-Carrera & García-Blanco, 1971) and the reader is referred to this article for a description of the structure and for illustrations. To facilitate comparison the same atom numbering has been used.

Due to the larger ionic radius of Pd^{2+} the metal–oxygen distances in PdB_2O_4 are longer than in CuB_2O_4. This also accounts for the increased lattice parameters of the Pd compound. Thereby, the Pd(1)—O distances determine the a lattice parameters, whereas the Pd(2)—O distances determine the increase in c. Since the corresponding Pd—O distances are not parallel to the a or c axes, the increases are not simply additive. The corresponding angles are 23 (1)° for O(1)—[Pd(1)]—O(1)′/[100] and 21 (1)° for O(4)—[Pd(2)]—O(4)′/[001].

Both Pd atoms have square-planar coordination. Pd(1) is situated on the $\bar{4}$ axis and corresponding to this point symmetry the four coordinating O atoms form a very flattened 'tetrahedron', with distances from a least-squares plane through these atoms of about 0·1 Å. The twofold axis passing through O(2), Pd(2) and O(3) forces the environment of Pd(2) to be ideally flat. Both least-squares planes make an angle of 69 (1)° with each other.

The distances in the boron–oxygen framework of the two isotypical compounds are nearly the same; only minor differences occur for the $B(1)$–O_4 tetrahedron, where the B(1)—O(1) and B(1)—O(4) bonds are slightly longer for the Pd compound.

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