Potassium Tetrabromopalladate(II)

By Don S. Martin Jr, John L. Bonte, Rhonda M. Rush and Robert A. Jacobson

Ames Laboratory of the USAEC and the Department of Chemistry,
Iowa State University, Ames, Iowa, 50010, *U.S.A.*

Abstract. Tetragonal, $P4/mmm$, $a=b=7\cdot409(12)$, $c=4\cdot309(7)$ Å; K_2PdBr_4, $Z=1$, $D_x=3\cdot54$ g cm^{-3}. The dark brown crystals were grown from the aqueous solution by evaporation. The structure, refined to $R=0\cdot040$, is isomorphous with K_2PtCl_4 with a Pd–Br distance of $2\cdot444(3)$ Å.

Introduction. A small, almost cubic crystal $(0\cdot187\times 0\cdot147\times 0\cdot147$ mm$)$ was mounted directly on a four-circle diffractometer interfaced with a PDP-15 computer [for further details see Schroeder & Jacobson (1973)]. The local *BLIND* (Jacobson, 1973) program was used to automatically index all reflections; a tetragonal cell was indicated and further confirmed *via* oscillation photographs around the three cell axes. In the data collection, each peak was centered in ω and two 2·5 s peak measurements were made offset by 0·01° in ω. Background measurements were also made for 2·5 s. Four octants $(hkl,\ hk\bar{l},\ h\bar{k}l,\ hkl)$ of data $(2\theta<50°)$ were taken yielding a total of 910 measured reflections. Graphite-monochromated Mo $K\alpha$ radiation was used $(\lambda=0\cdot7107)$. Three reflections were selected for standards and remeasured periodically to confirm that no detectable crystal decomposition occurred during the data collection. Data were corrected for Lorentz–polarization, and for absorption $(\mu=206\cdot7$ cm$^{-1})$ using the *ORABS* (Wehe, 1962) program. The structure factor errors were estimated with the formula:

$$\sigma(F)=\{[NET/T+\sigma(1)]/LP\}^{1/2}-F_o$$
where
$$\sigma(1)=[TC+BK+(0\cdot03TC)^2$$
$$+(0\cdot03BK)^2+(0\cdot03NET)^2]^{1/2} .$$

TC is the total intensity, BK background intensity, NET net intensity, LP Lorentz–polarization factor, T transmission factor. Reflections with $|F_o|<3\sigma(F_o)$ were considered unobserved. The $|F_o|$'s were averaged arithmetically for equivalent reflections and the related $\sigma(F)$ was calculated as $[\sum\limits_{i=1}^{N}\sigma_i^2(F)]^{1/2}/N$, where N is the number of observed reflections for a unique reflection to be averaged.

The initial positions of the palladium and bromine atoms were based on the analogous structure of K_2PtCl_4 (Mais, Owston & Wood, 1972). A Patterson map analysis confirmed the positions of these atoms. An electron density difference map indicated the position of the potassium atoms. The structural and thermal parameters were refined for 155 unique re-
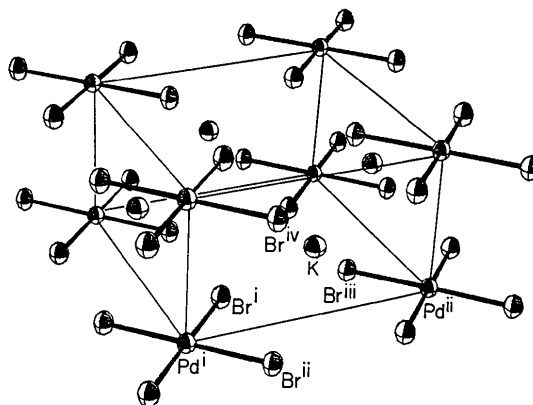

Fig. 1. Perspective view of the unit cell for K_2PdBr_4.

Table 1. *Final positional and thermal parameters*

Thermal parameters are of the form exp $[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\times10^{-4}]$. Numbers in parentheses refer to error of least significant digits.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}
Pd	0	0	0	89 (5)	89 (5)	337 (9)	*
K	0·5	0	0·5	135 (5)	135 (5)	404 (6)	*
Br	0·23323 (8)	0·23323(8)	0	105 (2)	105 (2)	509 (10)	−7 (1)

* By symmetry:
Pd$(x,y,z)=(0,0,0)$; $\beta_{11}=\beta_{22}\ne\beta_{33}$; $\beta_{12}=\beta_{13}=\beta_{23}=0$
K $(x,y,z)=(\frac{1}{2},0,\frac{1}{2})$; $\beta_{11}=\beta_{22}\ne\beta_{33}$; $\beta_{12}=\beta_{13}=\beta_{23}=0$
Br$(x,y,z)=(x,x,0)$; $\beta_{11}=\beta_{22}\ne\beta_{33}$; $\beta_{12}\ne\beta_{13}=\beta_{23}=0$

flections by a full-matrix least-squares program, *ORFLS* (Busing, Martin & Levy, 1963). The relativistic Hartree–Fock scattering factors of Doyle & Turner (1968) modified for the real and imaginary parts of anomalous dispersion (*International Tables for X-ray Crystallography*, 1968) were used. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. In this space group all atoms are in special positions, and only one bromine positional parameter could be varied. Anisotropic refinement converged to a final residual, $R = 0.077$, where $R = (\sum |F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$. At this stage of analysis the $|F_c|$'s of the ten strongest reflections were observed to be consistently greater than $|F_o|$, indicating the possibility of secondary extinction. To correct for isotropic secondary extinction the Coppens & Hamilton (1970) method with a modification of the *ORFLS* program was used and the extinction factor g introduced into the refinement. After a few cycles of additional refinement a plot of $\overline{w(|F_o| - |F_c|)^2}$ *vs* $|F_o|$ indicated a slight adjustment in weight was necessary for the larger reflections, and the weights were subsequently corrected. Refinement converged to $R = 0.040$, $R_w = 0.047$, $g = 0.019$, and a final electron density difference map indicated no peaks greater than 1.0 e Å^{-3}.

Final values of positional and thermal parameters are given in Table 1. Interatomic distances calculated from *ORFFE* (Busing, Martin & Levy, 1964) are given in Table 2.* A view of the unit cell drawn with *ORTEP* (Johnson, 1965) is shown in Fig. 1.

Discussion. Symmetry dictates that the $[PdBr_4]^{2-}$ units be exactly square planar (D_{4h} symmetry). The Br^i–Br^{ii} distance, 3·456 Å, for atoms in the same $[PdBr_4]^{2-}$ unit is shortened relative to that expected for bromide ions in an ionic lattice. This effect is due to coordinate-covalent bonding to the palladium atom. The Br^i–Br^{iii}

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31101 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Selected interatomic distances (Å) with standard deviations*

(See Fig. 1 for definition of symmetry equivalent atom.)

Pd^i–Br^i	2·444 (3)	Br^i–Br^{ii}	3·456 (6)
Pd^i–K	4·285 (6)	Br^i–Br^{iii}	3·953 (7)
Br^i–K	3·396 (3)	Br^{ii}–Br^{iv}	4·309 (7)

distance, 3·953 Å, however, for atoms on adjacent ionic units is virtually identical with the distance between two close-packed bromide ions in an ionic lattice, 3·90 Å (Douglas & McDaniel, 1965). The Pd^i–Br^i bond distance is virtually the same as the Pt–Br bond distance in the platinum analog (Kroening, Rush, Martin & Clardy, 1974).

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1963). *ORFLS.* Oak Ridge National Laboratory Report ORNL-TM-305.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE.* Oak Ridge National Laboratory Report ORNL-TM-306.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.

DOUGLAS, B. E. & McDANIEL, D. H. (1965). *Concepts and Models of Inorganic Chemistry*, p. 109. Waltham, Massachusetts: Blaisdell.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A24, 390–397.

International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., pp. 215–216. Birmingham: Kynoch Press.

JACOBSON, R. A. (1973). Abstracts, Amer. Cryst. Assoc. Summer Meeting. Vol. I, Series 2, p. 141.

JOHNSON, C. K. (1965). *ORTEP.* Oak Ridge National Laboratory Report ORNL-3794.

KROENING, R. F., RUSH, R. M., MARTIN, D. S. & CLARDY, J. C. (1974). *Inorg. Chem.* 13, 1366–1373.

MAIS, R. H. B., OWSTON, P. G. & WOOD, A. M. (1972). *Acta Cryst.* B28, 393–399.

SCHROEDER, D. R. & JACOBSON, R. A. (1973). *Inorg. Chem.* 12, 210–213.

WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *ORABS.* Oak Ridge National Laboratory Report ORNL-TM-229.