

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.054$
 $S = 0.704$
 423 reflections
 32 parameters
 $w = 1/[\sigma^2(F_o^2)]$
 $(\Delta/\sigma)_{\max} = 0.045$
 $\Delta\rho_{\max} = 1.64 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.63 \text{ e } \text{Å}^{-3}$

Extinction correction:
SHELXL97 (Sheldrick,
 1997a)
 Extinction coefficient:
 0.0055 (3)
 Scattering factors from
International Tables for
Crystallography (Vol. C)

gram(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b).
 Program(s) used to refine structure: *SHELXL97*. Molecular
 graphics: *ATOMS for Windows* (Dowty, 1995). Software used
 to prepare material for publication: *SHELXS97*.

We are grateful to Dr Claude Didierjean (Laboratoire
 de Cristallographie et Modelization des Matériaux
 Minéraux et Biologiques, Faculté des Sciences de
 Nancy I) for his help during the data reduction.

Supplementary data for this paper are available from the IUCr
 electronic archives (Reference: BR1251). Services for accessing these
 data are described at the back of the journal.

Table 1. Fractional atomic coordinates and equivalent
 isotropic displacement parameters (Å^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \cdot \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Er1	0	0.65375 (9)	1/4	0.0097 (2)
Er2	0.19927 (5)	0	0	0.0105 (2)
Ge3†	0	0.0408 (2)	1/4	0.0059 (15)
Ga4‡	0	0.0408 (2)	1/4	0.041 (12)
Ga5	0	0.32084 (17)	0.44813 (12)	0.0117 (3)
Ge6	0.20266 (12)	0.29135 (17)	1/4	0.0119 (3)

† Site occupancy = 0.787 (16). ‡ Site occupancy = 0.213 (16).

Table 2. Selected bond lengths (Å)

Er1—Ga5 ^I	2.8387 (11)	Ge3—Ge6 ^{VI}	2.6454 (17)
Er1—Ga5 ^{II}	2.8387 (11)	Ge3—Ga5	2.7878 (18)
Er1—Ge3 ^{III}	2.871 (2)	Ge3—Ga5 ^{VI}	2.7878 (18)
Er1—Ge6 ^{IV}	2.9443 (12)	Ge3—Er1 ^{XV}	2.871 (2)
Er1—Ge6 ^V	2.9443 (12)	Ge3—Er2 ^X	3.0033 (4)
Er1—Ga5 ^{VI}	3.0910 (13)	Ge3—Er2 ^{XVI}	3.0033 (4)
Er1—Ga5	3.0910 (13)	Ga5—Ge6 ^{VI}	2.6546 (12)
Er1—Ge6 ^{VII}	3.2817 (13)	Ga5—Ge6	2.6546 (12)
Er1—Ge6	3.2817 (13)	Ga5—Ga5 ^I	2.831 (2)
Er2—Ge6 ^{VIII}	2.9543 (8)	Ga5—Er1 ^I	2.8387 (11)
Er2—Ge6 ^{IX}	2.9543 (8)	Ga5—Er2 ^{XVI}	3.0540 (10)
Er2—Ge3 ^X	3.0033 (4)	Ga5—Er2 ^{XI}	3.0540 (10)
Er2—Ge3	3.0033 (4)	Ga5—Er2 ^{XVII}	3.1313 (7)
Er2—Ga5 ^{XI}	3.0540 (10)	Ga5—Er2 ^{XVIII}	3.1313 (7)
Er2—Ga5 ^{VI}	3.0540 (10)	Ge6—Ga5 ^{VI}	2.6546 (12)
Er2—Ga5 ^{XII}	3.1313 (7)	Ge6—Er1 ^{XIX}	2.9443 (12)
Er2—Ga5 ^{XIII}	3.1313 (7)	Ge6—Er2 ^{XVII}	2.9543 (8)
Er2—Ge6 ^{XIV}	3.1897 (9)	Ge6—Er2 ^{XVIII}	2.9543 (8)
Er2—Ge6	3.1897 (9)	Ge6—Er2 ^{XI}	3.1897 (9)
Ge3—Ge6	2.6454 (17)		

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, 1-y, z - \frac{1}{2}$; (iii) $x, 1+y, z$;
 (iv) $\frac{1}{2}-x, \frac{1}{2}+y, z$; (v) $-x - \frac{1}{2}, \frac{1}{2}+y, z$; (vi) $x, y, \frac{1}{2}-z$; (vii) $-x, y, z$; (viii)
 $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (ix) $\frac{1}{2}-x, y - \frac{1}{2}, z$; (x) $-x, -y, -z$; (xi) $-x, -y, z - \frac{1}{2}$;
 (xii) $\frac{1}{2}-x, \frac{1}{2}-y, z - \frac{1}{2}$; (xiii) $\frac{1}{2}+x, y - \frac{1}{2}, \frac{1}{2}-z$; (xiv) $x, -y, -z$;
 (xv) $x, y - 1, z$; (xvi) $-x, -y, \frac{1}{2}+z$; (xvii) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$; (xviii)
 $x - \frac{1}{2}, \frac{1}{2}+y, \frac{1}{2}-z$; (xix) $\frac{1}{2}+x, y - \frac{1}{2}, z$.

In the final electron-density difference map, both the minimum ($-1.63 \text{ e } \text{Å}^{-3}$ at 0.5, 0.1456, 0.347) and the maximum ($1.64 \text{ e } \text{Å}^{-3}$ at 0.4378, 0.0552, 0.5) peaks occur approximately 0.93 Å from the heavy Er1 atom. They are due to the irregular crystal shape and the empirical absorption correction method (*SORTAV*; Blessing, 1987). The *SHELXL97* (Sheldrick, 1997a) recommended weighting scheme ($a = 0, b = 0$) does not permit one to obtain a goodness-of-fit value close to 1.0. The low value of the least-squares goodness-of-fit is due to the data reduction procedure (*DENZO* and *SCALEPACK*; Otwinowski & Minor, 1997), which overestimates (by a factor of approximately 1.3) the standard deviation of the measured intensities.

Data collection: *COLLECT* (Nonius, 1998). Cell refinement: *COLLECT*. Data reduction: *DENZO* and *SCALEPACK*. Pro-

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The solid solution of composition $\text{K}_2\text{PdBr}_{2.24}\text{Cl}_{1.76}$

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Abstract

The structure of $\text{K}_2\text{PdBr}_{2.24}\text{Cl}_{1.76}$, dipotassium bromochloropalladate, an isotype of K_2PdCl_4 and K_2PdBr_4 , has been determined in the centrosymmetric space group *P4/mmm*. The tetragonal cell contains one Pd atom. The $[\text{PdX}_4]^{2-}$ ions ($X = \text{Cl}, \text{Br}$) are square planar, with Pd—X bond lengths of 2.3934 (9) Å.

Comment

The structure of K_2PdCl_4 has been determined by Mais *et al.* (1972) and that of K_2PdBr_4 by Martin *et al.* (1975). Our X-ray powder diffraction analyses of anhydrous $K_2PdCl_{4-x}Br_x$ ($0 < x < 4$) solid solutions have demonstrated that these compounds are isotypes of both potassium tetrachloropalladate(II) and potassium tetrabromopalladate(II), which crystallize in the tetragonal system with the $P4/mmm$ space group. In the present work, we report the crystal structure refinement of the solid solution of composition $K_2PdBr_{2.24}Cl_{1.76}$ (Fig. 1). The refinement shows unambiguously that Br and Cl atoms occupy the same site X (4j). The Pd—X distances [2.3934 (9) Å] are intermediate between those obtained previously for Pd—Cl [2.313 (1) Å] in K_2PdCl_4 (Mais *et al.*, 1972) and Pd—Br [2.444 (1) Å] in K_2PdBr_4 (Martin *et al.*, 1975).

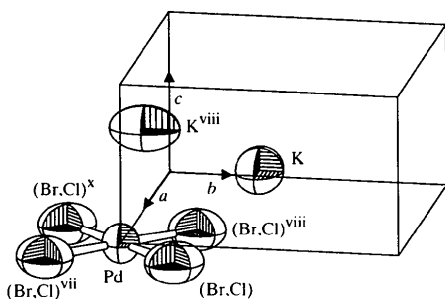


Fig. 1. A view of the asymmetric unit of $K_2PdBr_{2.24}Cl_{1.76}$. Displacement ellipsoids are shown at the 90% probability level. [Symmetry codes: (vii) $-x, -y, -z$; (viii) $y, -x, -z$; (x) $-y, x, z$.]

Experimental

Crystals of $K_2PdBr_{2.24}Cl_{1.76}$ were prepared by dissolving commercial powders of K_2PdCl_4 and K_2PdBr_4 (Fluka purissimum) in aqueous HCl ($M/10$). The concentration was 0.005 mol l^{-1} in K_2PdCl_4 and K_2PdBr_4 , and the solution was evaporated slowly in a furnace at 353 K. After complete crystallization, yellow-ochre to red-brown crystals were obtained and preserved in a desiccator over P_4O_{10} . A single crystal was then sealed in a Lindemann glass capillary.

Crystal data

$K_2PdBr_{2.24}Cl_{1.76}$

$M_r = 425.99$

Tetragonal

$P4/mmm$

$a = 7.237 (1) \text{ \AA}$

$c = 4.208 (1) \text{ \AA}$

$V = 220.39 (7) \text{ \AA}^3$

$Z = 1$

$D_x = 3.210 \text{ Mg m}^{-3}$

D_m not measured

Ag $K\alpha$ radiation

$\lambda = 0.56087 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 5\text{--}15^\circ$

$\mu = 7.236 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Parallelepiped

$0.02 \times 0.02 \times 0.02 \text{ mm}$

Dark brown

Data collection

Enraf-Nonius CAD-4 diffractometer

$R_{int} = 0.048$

$\theta_{max} = 24.72^\circ$

ω/θ scans

Absorption correction: none

434 measured reflections

237 independent reflections

203 reflections with

$I > 2\sigma(I)$

$h = 0 \rightarrow 8$

$k = 0 \rightarrow 8$

$l = 0 \rightarrow 6$

2 standard reflections

frequency: 180 min

intensity decay: 0.1%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.076$

$S = 1.189$

237 reflections

16 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 0.1055P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 1.79 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -1.15 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL97

Extinction coefficient:

0.011 (6)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$					
	Occupancy	x	y	z	U_{eq}
K	1	0	1/2	1/2	0.0432 (6)
Pd	1	0	0	0	0.0220 (3)
Br	0.56 (3)	0.23385 (8)	0.23385 (8)	0	0.0353 (18)
Cl	0.44 (6)	0.23385 (8)	0.23385 (8)	0	0.027 (5)

Table 2. Selected bond lengths (\AA)

K—Cl/Br ($\times 8$) 3.3168 (4) Pd—Cl/Br ($\times 4$) 2.3934 (9)

With the aim of limiting the time of the experiment and considering the number of refined parameters (16), the reflections were collected as indicated in the *Data collection* section (completeness $\approx 88\%$). In the final electron-density difference map, the minimum [-1.15 e \AA^{-3} at (0,0,0.208)] and maximum [1.79 e \AA^{-3} at (0,0,0)] peaks occur at 0.88 and 0.00 Å from the Pd atom, respectively.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CADAK* (Sheldrick, 1987). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ATOMS for Windows* (Dowty, 1995). Software used to prepare material for publication: *SHELXL97*.

We are grateful to Dr Claude Didierjean (Laboratoire de Cristallographie et Modelisation des Materiaux Mineraux et Biologiques, Faculté des Sciences de Nancy I) for his help during the data reduction.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1258). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C55, 1972–1974

Na₂NbO₂AsO₄, a new niobium monoarsenate

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Abstract

The two-dimensional framework of disodium dioxoniobium arsenate is built up from infinite [NbO₆] chains extending along the *c* axis, linked together by AsO₄ tetrahedra. Each AsO₄ tetrahedron is bonded to three different NbO₆ octahedra, two of which belong to the same chain. The Na⁺ cations are located between the covalent [NbAsO₆]²⁻ layers in hexagonal channels. The structure is compared with those of MM'XO₆ (*M* = K, Tl; *M'* = Sb, Nb; *X* = P, As) and NaVOAsO₄.

Comment

In the course of our investigation of the Na₂O–Nb₂O₅–As₂O₅ system, in a search for open framework structures, we have reported previously the tunnel compound Na₃NbO(AsO₄)₂ (Hizaoui *et al.*, 1999). The present report deals with a new compound found in the same system, *i.e.* Na₂NbO₂AsO₄. Dioxoniobium disodium arsenate has a layer structure, built up from chains of *trans*-corner-sharing NbO₆ octahedra with alternating short and long Nb—O bonds; Nb—O⁵ = 1.882 (2) Å and Nb—O^{5'} = 2.012 (2) Å [symmetry code: (i) *x*, 1 – *y*, $\frac{1}{2}$ + *z*]. These infinite chains are interconnected laterally in the (100) plane by AsO₄ tetrahedra (Fig. 1). Each AsO₄ tetrahedron bridges two successive NbO₆ octahedra of the same chain by sharing O2 and O3 atoms, and bridges a third NbO₆ octahedron of an adjacent chain through O4. The free O-atom apices, O1 and O6, point alternately up and down the layers. This arrangement of polyhedra delimits distorted hexagonal windows connecting the interlayer spaces. In two suc-

cessive layers related by the 2₁ axis, the windows form tunnels parallel to the [101] and $[\bar{1}01]$ directions, where the Na³⁺ cations reside (Fig. 2). The Na¹⁺ and Na²⁺ cations are located in the interlayer space. The NbO₆ octahedra are slightly distorted, as in many niobium(V) arsenates; the Nb—O bond lengths range from 1.765 (2) to 2.210 (2) Å [average 2.050 (2) Å]. The AsO₄ tetrahedron is almost regular, with As—O distances ranging from 1.652 (2) to 1.705 (2) Å and O—As—O angles ranging from 108.2 (1) to 113.5 (1)°. As is usual in most condensed arsenate ions, the unshared O atom, O1, forms a shorter bond than the other three O atoms. The bond-valence sums (Brown & Altermatt, 1985) for the Nb^V and As^V atoms of 5.042 and 4.984, respectively, are in good agreement with their formal oxidation states. The Na₂NbO₂AsO₄ structure exhibits a relationship with K₂SbPO₆ (Lachgar *et al.*, 1986), K₂SbAsO₆ (Botto & Garcia, 1989) and NaVOAsO₄ (Haddad *et al.*, 1992). Indeed, one can pass from the structure of K₂SbPO₆ (one-dimensional) to that of Na₂NbO₂AsO₄ (two-dimensional) by separating one of the two O atoms of the edge shared between successive SbO₆ octahedra and forming an Sb—O—P bridge with neighbouring chains. The structure of NaVOAsO₄ (three-dimensional) can be derived from that of Na₂NbO₂AsO₄ (two-dimensional) by forming mixed Nb—O—As bridges between successive layers; the O1 apex is shared with the O6 apex, leading to the elimination of one O atom. Electrical neutrality requires the removal of two Na⁺ cations from the interlayer space. Comparison with the analogous compound Tl₂NbPO₆ (Fakhfak *et al.*, 1993) shows that Na₂NbO₂AsO₄ and Tl₂NbPO₆ are both two-dimensional compounds; the two structures differ in the type of connection between the polyhedra.

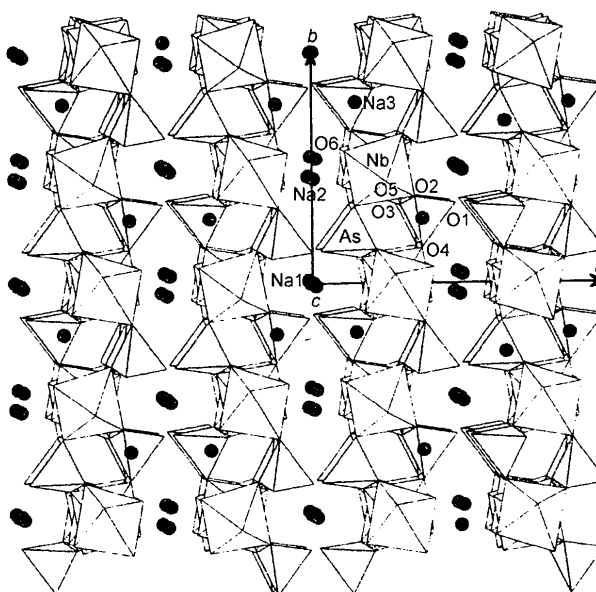


Fig. 1. DIAMOND (Bergerhoff, 1996) view along the *c* axis of the crystal structure of Na₂NbO₂AsO₄.