References

Eichhorn, B. W. (1994). *Progress in Inorganic Chemistry*, Vol. 42, edited by K. D. Karlin, pp. 139–237. New York: John Wiley & Sons.

Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.

Gardner, D. R., Fettinger, J. C. & Eichhorn, B. W. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 1859–1860.

Gardner, R. A., Vlasse, M. & Wold, A. (1969). *Acta Cryst.* B**25**, 781–787.

Gotoh, Y., Goto, M., Kawaguchi, K., Oosawa, Y. & Onoda, M. (1990). *Mater. Res. Bull.* **25**, 307–314.

Gotoh, Y., Onoda, M., Goto, M. & Oosawa, Y. (1989). *Chem. Lett.* pp. 1281–1282.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Krebs, B., Buss, B. & Ferwanah, A. (1972). *Z. Anorg. Allg. Chem.* **387**, 142–153.

Lundquest, D. & Westgren, A. (1936). *Sven. Kem. Tidskr.* **4**, 241.

Müller, A. & Diemann, E. (1969). *Chem. Ber.* **102**, 2044–2049.

Murugesan, T., Ramesh, S., Gopalakrishnan, J. & Rao, C. N. R. (1981). *J. Solid State Chem.* **38**, 165–172.

Onoda, M. & Kato, K. (1990). *Acta Cryst.* B**46**, 487–492.

Ouvrard, G., Tchangbedji, G., Deniard, P. & Prouzet, E. (1995). *J. Power Sources*, **54**, 246–249.

Pauling, L. & Hultgren, R. (1933). *Z. Kristallogr.* **84**, 204–206.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1994). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Tranchitella, L. J., Fettinger, J. C. & Eichhorn, B. W. (1996). *Chem. Mater.* In the press.

Van den Berg, J. M. & DeVries, R. (1964). *Proc. K. Ned. Akad. Wet.* B**67**, 178–179.

Acta Cryst. (1997). C**53**, 165–167

K₂WSe₄

DANIEL RÖHNERT, CHRISTIAN NÄTHER AND WOLFGANG BENSCH

Institut für Anorganische Chemie der Universität Frankfurt, Marie-Curie-Strasse 11, 60439 Frankfurt/Main, Germany. E-mail: bensch@chemie.uni-frankfurt.de

Abstract

The crystal structure of dipotassium tungsten tetraselenide is based on isolated, slightly distorted WSe_4 tetrahedra joined *via* K^+ ions. The compound is isotypic with the previously reported Rb and Cs analogues and crystallizes in the β-K_2SO_4 structure type.

Comment

Ternary alkali metal tungsten chalcogenides A_2WQ_4 (A = Rb, Cs, NH_4^+; Q = S, Se) have been prepared

using classical solution chemistry (Müller & Sievert, 1974; Müller, Diemann & Heidborn, 1970). The crystal structures of these compounds were reported about 20 years ago. It is interesting to note that these preparation methods did not lead to the successful synthesis of the potassium selenide. During our research on the preparation of new tungsten chalcogenides using the so-called 'reactive flux' method (Sunshine, Kang & Ibers, 1987; Kanatzidis & Sutorik, 1995), the previously unknown ternary tungsten selenide K_2WSe_4 was obtained. It is most likely that conventional preparation methods, either in aqueous solution or at high temperatures, are destined to favour the thermodynamically more stable binary compounds (Kanatzidis, 1990).

The structure of K_2WSe_4 consists of slightly distorted WSe_4^{2-} tetrahedra located on crystallographic mirror planes, with W—Se bond lengths ranging from $2.3050\,(7)$ to $2.3266\,(9)$ Å and Se—W—Se angles between $107.16\,(4)$ and $111.79\,(4)°$. These data are within the range reported for other ternary tungsten tetraselenides (Müller, Krebs & Beyer, 1968). The K^+ ions are coordinated by eight and nine Se centres with K—Se distances between $3.263\,(2)$ and $3.722\,(3)$ Å (Fig. 1). The coordination sphere of K1 (CN = 9) is of
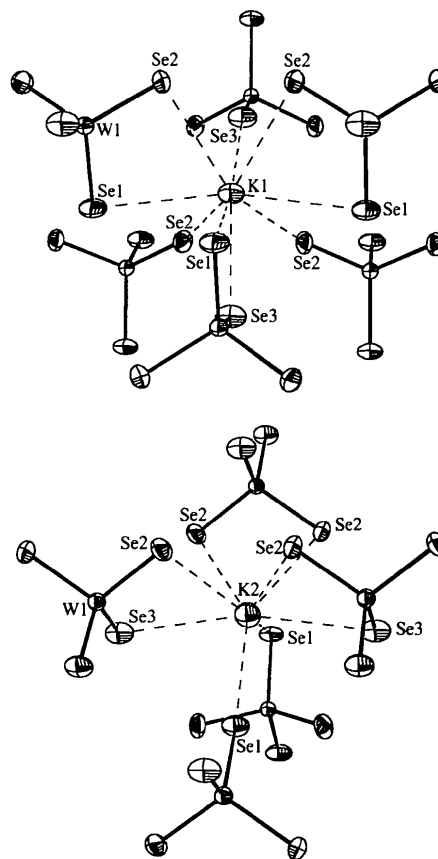

Fig. 1. The coordination spheres of K1 and K2 in K_2WSe_4. Displacement ellipsoids are plotted at the 50% probability level.

irregular shape whereas K2 (CN = 8) is located within a distorted bis-disphenoid.

The K2Se₈ polyhedra share edges with three WSe_4^{2-} tetrahedra and have common corners with two WSe_4^{2-} units. The K1Se₉ polyhedra are connected to three WSe_4^{2-} tetrahedra via edges and to three others via corners. As expected, the lattice parameters are smaller than those reported for the analogous Rb and Cs compounds (Table 3) (Müller & Sievert, 1974).

Experimental

Single crystals of K₂WSe₄ suitable for X-ray investigation were synthesized by heating a mixture of K₂Se₃, Se and W (molar ratio 3:6:1, prepared in a glove box) in sealed and evacuated (10^{-4} bar; 1 bar = 10^5 Pa) glass ampoules over a period of 5 d at 623 K. The crystals were grown by slow cooling of the ampoule (3 K h^{-1}). The friable dark red slabs were manually selected from the melt. K₂WSe₄ is soluble in polar solvents like DMF or acetonitrile. The crystals are moisture-sensitive and decompose within approximately 4 d, and were therefore coated with epoxy glue before being mounted for analysis.

Crystal data

K₂WSe₄	Mo $K\alpha$ radiation
$M_r = 577.89$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 94
$Pnma$	reflections
$a = 9.7337(8)$ Å	$\theta = 17$–$24.5°$
$b = 7.2012(6)$ Å	$\mu = 30.414$ mm^{-1}
$c = 12.5976(12)$ Å	$T = 293(2)$ K
$V = 883.02(13)$ Å^3	Slab
$Z = 4$	$0.48 \times 0.22 \times 0.05$ mm
$D_x = 4.347$ Mg m^{-3}	Dark red
D_m not measured	

Data collection

Stoe AED-II diffractometer	$R_{int} = 0.0362$
ω–2θ scans	$\theta_{max} = 29.99°$
Absorption correction:	$h = 0 \rightarrow 13$
numerical	$k = -10 \rightarrow 1$
$T_{min} = 0.0072$, $T_{max} =$	$l = -2 \rightarrow 17$
0.2196	4 standard reflections
1752 measured reflections	frequency: 120 min
1381 independent reflections	intensity decay: neglible

Refinement

Refinement on F^2	$\Delta\rho_{max} = 2.33$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.032$	$\Delta\rho_{min} = -2.48$ e Å^{-3}
$wR(F^2) = 0.086$	Extinction correction:
$S = 1.026$	SHELXL93 (Sheldrick,
1381 reflections	1993)
41 parameters	Extinction coefficient:
$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2]$	0.0078 (4)
where $P = (F_o^2 + 2F_c^2)/3$	Scattering factors from
$(\Delta/\sigma)_{max} = 0.001$	International Tables for Crystallography (Vol. C)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
K1	0.4537 (2)	1/4	0.3422 (2)	0.0399 (5)
K2	0.1574 (2)	1/4	0.6157 (3)	0.0501 (7)
W1	0.74805 (3)	1/4	0.56811 (3)	0.02196 (14)
Se1	0.51526 (8)	1/4	0.61001 (9)	0.0388 (3)
Se2	0.85321 (7)	0.50758 (10)	0.64021 (8)	0.0427 (2)
Se3	0.78380 (10)	1/4	0.38718 (9)	0.0428 (3)

Table 2. *Selected geometric parameters (Å, °)*

K1—Se3	3.263 (2)	K2—Se3^{iii}	3.6460 (5)
K1—Se3^i	3.329 (3)	K2—Se3^{vi}	3.6460 (5)
K1—Se1	3.427 (3)	K2—Se2^{ii}	3.667 (3)
K1—Se2^{ii}	3.467 (2)	K2—Se2^{iii}	3.667 (3)
K1—Se2^{iii}	3.467 (2)	K2—Se1^{ix}	3.722 (3)
K1—Se2^{iv}	3.613 (2)	K2—W1^{viii}	4.029 (2)
K1—Se2^v	3.613 (2)	K2—W1^{ix}	4.080 (3)
K1—Se1^{iii}	3.6632 (6)	K2—K1^x	4.719 (3)
K1—Se1^{vi}	3.6632 (6)	W1—Se2	2.3050 (7)
K2—Se1	3.484 (2)	W1—Se2^{xi}	2.3050 (7)
K2—Se2^{vii}	3.507 (2)	W1—Se3	2.3056 (12)
K2—Se2^{viii}	3.507 (2)	W1—Se1	2.3266 (9)
Se2—W1—Se2^{xi}	107.16 (4)	Se2—W1—Se1	110.07 (3)
Se2—W1—Se3	108.82 (3)	Se2^{xi}—W1—Se1	110.07 (3)
Se2^{xi}—W1—Se3	108.82 (3)	Se3—W1—Se1	111.79 (4)

Symmetry codes: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (ii) $1 - x, y - \frac{1}{2}, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$; (v) $\frac{3}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (vi) $1 - x, -y, 1 - z$; (vii) $x - 1, \frac{1}{2} - y, z$; (viii) $x - 1, y, z$; (ix) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (x) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (xi) $x, \frac{1}{2} - y, z$.

Table 3. *Comparison of the lattice parameters (Å) and cell volumes (Å^3) of K₂WSe₄, Rb₂WSe₄ and Cs₂WSe₄*

	a	b	c	V
K₂WSe₄	9.734 (1)	7.201 (1)	12.598 (1)	883.02 (13)
Rb₂WSe₄	10.10	7.28	12.85	944.7
Cs₂WSe₄	10.32	7.45	13.07	1004.5

The data were corrected for Lorentz and polarization effects. All atoms were refined with anisotropic displacement parameters. The largest peaks in the difference map are located in the neighbourhood of W1. It is noted that most of the atoms in special positions show significantly higher values for U^{22} than for the other displacement components, indicating possible disorder which could not be resolved during this study. Such disorder is well documented for different compounds with the β-K₂SO₄ structure.

Data collection: *DIF4* (Stoe & Cie, 1992). Cell refinement: *DIF4*. Data reduction: *DIF4*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXL93 CIFTAB*.

References

Kanatzidis, M. (1990). *Chem. Mater.* **2**, 353–363.

Kanatzidis, M. & Sutorik, A. (1995). *Prog. Inorg. Chem.* **43**, 151–265.

Müller, A., Diemann, E. & Heidborn, U. (1970). *Z. Anorg. Allg. Chem.* **376**, 125–133.

Müller, A., Krebs, B. & Beyer, H. (1968). *Z. Naturforsch.* **236**, 1537–1538.

Müller, A. & Sievert, W. (1974). *Z. Anorg. Allg. Chem.* **498**, 251–266.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement.* University of Göttingen, Germany.

Sheldrick, G. M. (1995). *SHELXTL/PC.* Version 5.04. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stoe & Cie (1992). *DIF4. Diffractometer Control Program.* Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.

Sunshine, S. A., Kang, D. & Ibers, J. A. (1987). *J. Am. Chem. Soc.* **109**, 6202–6204.

A New Polymorph of Li4P2O7

ABDELAALI DAIDOUH,[a] MARIA L. VEIGA,[a] CARLOS PICO[a] AND MARTIN MARTINEZ-RIPOLL[b]

[a]*Departamento de Quimica Inorganica I, Facultad de Ciencias Quimicas, Universidad Complutense de Madrid, E-28040 Madrid, Spain, and* [b]*Departamento de Cristalografia, Instituto de Quimica-Fisica Rocasolano-CSIC, Serrano 119, E-28006 Madrid, Spain. E-mail: xmartin@roca.csic.es*

Abstract

The purpose of the present paper is to report the crystal structure of a new phase of tetralithium diphosphate identified by single-crystal X-ray diffraction. The structure consists of layers built from Li–O tetrahedra and pyrophosphate groups connected to each other through edges and vertices.

Comment

A tetralithium diphosphate obtained by hydrothermal treatment at 1000 atm (1 atm = 101 325 Pa) for 100 h with four formula units of $Li_4P_2O_7$ in a $P2_1/n$ cell of dimensions $a = 5.190\,(2)$, $b = 13.902\,(3)$, $c = 7.901\,(3)$ Å, $\beta = 89.97\,(3)°$ was described recently (Yakubovich & Mel'nikov, 1994). The structure was described as the first lithium phosphate structure containing diphosphate groups formed by vertex-sharing PO_4 tetrahedra (see also Wenger & Armbruster, 1991; Tien & Hummel, 1961; Keffer, Mighell, Mauer, Swanson & Block, 1967; Averbuch-Pouchot & Durif, 1986). Comparison of the present structure with that described by Yakubovich & Mel'nikov (1994) is not possible as the published coordinates of the latter appear to contain errors.

The new phase reported here (Fig. 1) can be described in terms of P_2O_7 and LiO_4 units. The pyrophosphate groups (lower right-hand side of Fig. 1), built up from two PO_4 tetrahedra sharing a vertex, show typical geometry with two long P—O bonds [P1—O1 1.622 (1) and P2—O1 1.626 (1) Å] corresponding to the P—O—P bridge and three shorter P—O bonds in the range 1.504 (1) to 1.527 (1) Å (Leclaire, Benmoussa, Borel, Grandin & Raveau, 1988; Constentin, Borel, Grandin, Leclaire & Raveau, 1990). The LiO_4 tetrahedra are highly distorted with Li—O distances ranging from
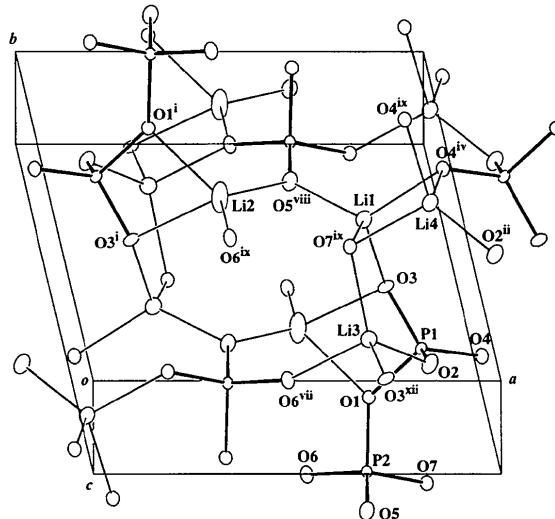

Fig. 1. Projection of the structure on the *ab* plane showing the atom labels. Displacement ellipsoids are represented at the 50% probability level. Symmetry codes: (i) 1 −*x*, 1−*y*, 1−*z*; (ii) 2 −*x*, 1−*y*, 2−*z*; (iv) 2 −*x*, 1−*y*, 1−*z*; (vii) 1 −*x*, −*y*, 1−*z*; (viii) *x*, 1 + *y*, *z*; (ix) *x*, 1 + *y*, 1 + *z*; (xii) *x*, *y*, 1 + *z*.
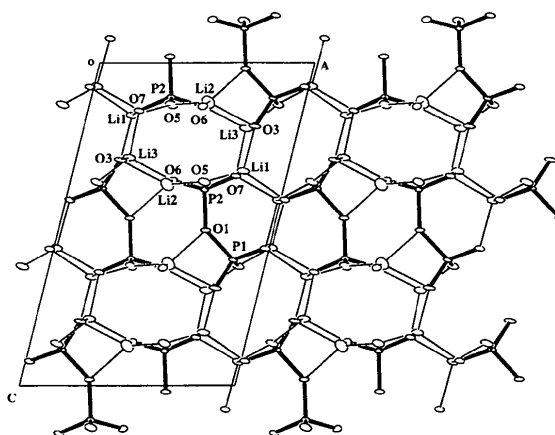

Fig. 2. The structure as drawn along the *b* axis of the pseudo monoclinic *A*-centred cell. All possible twofold axes appearing along **b** are destroyed by the relative situation of the P2—O5 and Li2—O6 bonds around them. See, for instance, the pseudo-twofold axis perpendicular to the eight-membered rings formed by the labelled atoms.