

**Discussion.** The molecule (Fig. 1) possesses approximate  $C_2$  symmetry, the twofold axis bisecting the S—S bond. The piperidine rings adopt the chair conformation, and the N atoms are pyramidal, although the relatively large C—N—S angles (mean  $116.0^\circ$ ) may imply some N—S  $\pi$  interaction. Hordvik (1966) has proposed an empirical correlation between S—S distances and X—S—S—X dihedral angles. Dipiperidine disulphide and dimorpholine disulphide (which has a similar molecular but different crystal structure; Nyburg & Pickard, 1973) are not in good accord with this correlation, although it should be noted that Hordvik's conclusions were based primarily on C—S—S—C systems. There are two unusually short intermolecular contacts [H(5)··S(1a) 2.97; H(3')··S(1b) 2.88 Å; S(1a) is generated from S(1) by the symmetry transformation  $-x, -\frac{1}{2} + y, \frac{1}{2} - z$  and

S(1b) by  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ], but these may be influenced by the geometrical constraints applied to the H atoms.

We are grateful to the Science Research Council for a contribution towards the cost of the diffractometer, and for a maintenance grant to PCM. The calculations were performed on the Cambridge University IBM 370/165 computer with programs written by GMS.

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## Raspite from Broken Hill

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**Abstract.**  $PbWO_4$ , monoclinic,  $P2_1/a$ ,  $a = 13.555$  (11),  $b = 4.976$  (2),  $c = 5.561$  (3) Å,  $\beta = 107.63$  (7)°,  $Z = 4$ ,  $D_x = 8.45$  g cm<sup>-3</sup>. Crystals were found in Broken Hill, NSW, Australia. Topotactic relations to the scheelite-type form of  $PbWO_4$  (stolzite) were found. The coordination number of W is six and  $WO_6$  octahedra form a chain by edge sharing. Pb is coordinated to seven O atoms.

**Introduction.** Although the colour (deep brown) of the crystals and the description by Palache, Berman & Frondel (1966) suggested the existence of impurities such as Fe and Mn in the compound, none were detected by electron-probe X-ray microanalysis with a JEOL instrument. The possible impurities are present to less than 500 p.p.m.

A crystal about  $230 \times 100 \times 40$   $\mu\text{m}$  was used for the structure analysis. The intensity data were collected on a Rigaku four-circle diffractometer with  $Mo K\alpha_1$  ( $\lambda = 0.70926$  Å) radiation monochromatized by graphite. In the range of  $2\theta \leq 60^\circ$ , 3998 independent reflexions were measured of which 1854 reflexions were considered unobserved. The systematic absences were  $h0l$ ,  $h = 2n + 1$  and  $0k0$ ,  $k = 2n + 1$ , indicating the space group  $P2_1/a$  (No. 14). An absorption correction was applied to the observed data ( $\mu = 801.6$  cm<sup>-1</sup>).

The positions of the Pb and W atoms were obtained by the Patterson superposition method. A successive Fourier synthesis revealed the positions of the O atoms. In the subsequent full-matrix least-squares refinement with the program *ORFLS* (Busing, Martin & Levy, 1962), the temperature factors of the Pb and W atoms were assumed to be anisotropic. The  $R$  value converged to 0.080 and the weighted  $R$  to 0.092 for 2144 observed reflexions.\* The atomic scattering factors were taken from Hanson, Herman, Lea & Skillman (1964).

**Discussion.** All the known  $AWO_4$  tungstates of which the divalent A cation is larger than  $Ca^{2+}$  crystallize under normal conditions in the scheelite-type structure. At higher pressure, new phases were found in  $PbWO_4$  (Chang, 1971) and  $BaWO_4$  (Fujita, Yamaoka & Fukunaga, 1974). The high-pressure form of  $BaWO_4$  ( $BaWO_4$ -II) has a characteristic dense structure (Kawada, Kato & Fujita, 1974), and that of  $PbWO_4$  is

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32000 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

isomorphous with BaWO<sub>4</sub>-II (Fujita, Yamaoka, Fukunaga, Kato & Kawada, 1975; Richter, Kruger & Pistorius, 1976). Raspite is another distinct form of PbWO<sub>4</sub> which has not been successfully prepared in the laboratory. Concerning the structure of this mineral, only a brief analysis was carried out by Shaw & Claringbull (1955) and some relations to the scheelite-type structure were suggested. Despite their different setting of the crystallographic axis, the *x* and *z* coordinates of the Pb and the W atoms reported by them are essentially the same as those found in the present work (Claringbull, 1974).

Tables 1 and 2 list the positional and the thermal parameters. Projections along the *a* and *b* axes are shown in Figs. 1 and 2. For simplicity, only the atoms

between  $-\frac{1}{4} < x < \frac{1}{4}$  are shown in Fig. 1. As depicted in the figures, each W atom is coordinated by six O atoms. Slightly distorted WO<sub>6</sub> octahedra form a chain parallel to [010] by sharing edges with each other. The Pb atom is coordinated to seven O atoms and its coordination polyhedron is rather irregular in shape.

In the scheelite structure, W atoms are in tetrahedral sites and isolated from each other, whereas in raspite, they approach each other along the *c* axis and two W atoms share two O atoms to form a chain of edge-shared octahedra. In spite of the very small volume difference of 0.53% between the two forms, the difference in the cation coordination is remarkable. The packing of the O atoms, however, can be regarded as

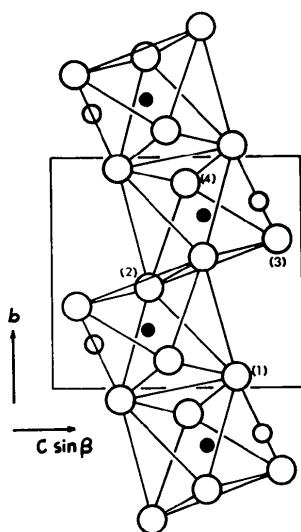


Fig. 1. Projection of the structure of raspite along the *a* axis. Atoms between  $-\frac{1}{4} < x < \frac{1}{4}$  are depicted. Large open circles denote O, small open circles Pb and small solid circles W. Independent O atoms are identified by the numbers in parentheses.

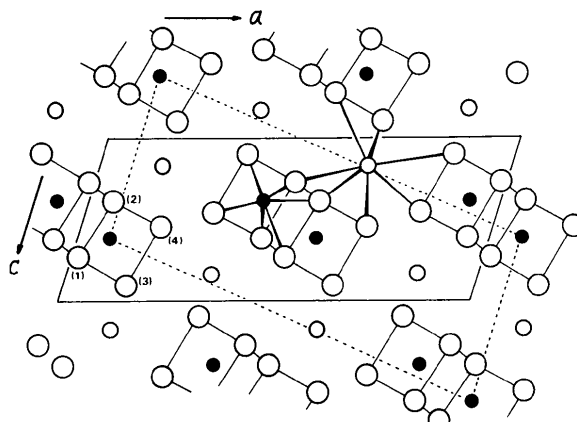


Fig. 2. Projection along the *b* axis. The atoms are depicted as in Fig. 1.

Table 1. Atomic coordinates ( $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>
Pb	1496.1 (0.8)	1940.5 (2.4)	1667.0 (2.1)
W	770.8 (0.7)	7494.4 (2.4)	6118.5 (1.9)
O(1)	163 (13)	515 (40)	7290 (35)
O(2)	595 (14)	4346 (44)	3882 (40)
O(3)	1510 (16)	6148 (50)	9000 (46)
O(4)	1903 (15)	8829 (47)	5386 (42)

Table 2. Thermal parameters

Anisotropic thermal parameters are of the form:  
 $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .  
 Values are multiplied by  $10^5$ .

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Pb	126 (4)	1124 (35)	991 (22)	25 (10)	191 (8)	-46 (24)
W	59 (3)	531 (28)	682 (19)	10 (9)	84 (7)	25 (23)

Isotropic thermal parameters of oxygen

O(1)	0.68 (22)	O(2)	0.95 (25)
O(3)	1.42 (32)	O(4)	1.10 (27)

Table 3. Interatomic distances between cations and oxygen atoms (Å)

	Pb-O		W-O
O(3 <sup>i</sup> )	2.65 (2)	O(3 <sup>iii</sup> )	2.17 (2)
O(3 <sup>ii</sup> )	2.77 (2)	O(3 <sup>v</sup> )	1.92 (2)
O(4)	2.31 (2)	O(4)	1.97 (2)
O(5 <sup>i</sup> )	2.68 (3)	O(4 <sup>iii</sup> )	2.07 (2)
O(5 <sup>vi</sup> )	2.85 (2)	O(5)	1.70 (2)
O(6 <sup>iv</sup> )	2.51 (2)	O(6)	1.83 (2)
O(6 <sup>v</sup> )	2.47 (2)	Average	1.94
Average	2.61	W-W <sup>iii</sup>	3.241 (2)
Next nearest neighbour O(5 <sup>vii</sup> )	3.13 (3)		

Symmetry code

(i)	<i>x</i> , <i>y</i> , 1 - <i>z</i> ;	(v)	<i>x</i> , 1 + <i>y</i> , <i>z</i>
(ii)	- <i>x</i> , - <i>y</i> , 1 - <i>z</i> ;	(vi)	$\frac{1}{2}$ - <i>x</i> , $-\frac{1}{2}$ - <i>y</i> , 1 - <i>z</i>
(iii)	- <i>x</i> , 1 - <i>y</i> , 1 - <i>z</i> ;	(vii)	<i>x</i> , -1 + <i>y</i> , -1 + <i>z</i>
(iv)	<i>x</i> , -1 + <i>y</i> , <i>z</i> ;		

Table 4. Bond angles ( $^{\circ}$ ) around the W atom ( $\angle O-W-O$ )

For symmetry code see Table 3.

	O(3 <sup>v</sup> )	O(4)	O(4 <sup>iii</sup> )	O(5)	O(6)
O(3 <sup>iii</sup> )	75.1 (0.8)	83.4 (0.8)	85.2 (0.7)	171.0 (1.0)	86.9 (0.8)
O(3 <sup>v</sup> )		148.7 (0.7)	82.6 (0.8)	96.8 (1.0)	105.5 (0.9)
O(4)			73.2 (1.0)	105.6 (1.0)	95.6 (0.9)
O(4 <sup>iii</sup> )				97.7 (1.0)	166.9 (0.9)
O(5)					91.7 (1.0)

essentially the same. The topotactic relation to the scheelite type is indicated in Fig. 2, where dotted lines show the scheelite-like unit cell. The following relations exist between the two unit cells:  $\mathbf{a}_r = -\mathbf{b}_s + \mathbf{c}_s$ ,  $\mathbf{b}_r = \mathbf{a}_s$ ,  $\mathbf{c}_r = \mathbf{b}_s$  ( $r$  raspite,  $s$  scheelite-like).

It is expected from these facts that the irreversible phase transformation (Shaw & Claringbull, 1955) from raspite to stolzite, the scheelite-type modification of  $PbWO_4$ , may be of displacive character. The displacements of the O atoms are small while those of the cations are relatively large.

Bond lengths and bond angles are listed in Tables 3 and 4 respectively. They were calculated with the program *ORFFE* (Busing, Martin & Levy, 1964). All the calculations for this study were carried out on the FACOM 270-20 of the National Institute for Researches in Inorganic Materials.

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### *o*-Aminophenylarsonic Acid

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**Abstract.**  $C_6H_8O_3NAs$ , monoclinic,  $P2_1$ ,  $a = 8.44$  (2),  $b = 4.93$  (2),  $c = 10.33$  (2) Å,  $\beta = 110.6$  (2) $^{\circ}$ ;  $M_r = 217.04$ ,  $Z = 2$ ,  $D_x = 1.78$ ,  $D_m = 1.79$  g cm $^{-3}$ . The structure was determined by the heavy-atom method and refined by least squares to an  $R$  of 0.086 for 628 observed reflexions measured from equi-inclination Weissenberg photographs. Molecules are linked together through O—H $\cdots$ O hydrogen bonds around the twofold screw axis. The As atom is tetrahedrally connected to two OH groups, O(2) and C(1)

of the benzene ring, the average tetrahedral angle around it being 109 $^{\circ}$  24'.

**Introduction.** Crystals of *o*-aminophenylarsonic acid (I) suitable for X-ray structural analysis were obtained from a mixture of water and alcohol. Cell constants were determined from oscillation and Weissenberg photographs taken with Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å). The Weissenberg photographs showed systematic absences corresponding to space groups  $P2_1$  and