Table 2. *Hydrogen-bond distances and angles*

	Position of acceptor atom			Distances (Å)		Angles (°)
				$D\cdots A$	$H\cdots A$	D–$H\cdots A$
N(1*A*)–H(1*A*)···O(8)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	2·670 (3)	1·83 (3)	174 (3)
N(1*B*)–H(1*B*)···O(6)	$x-1$,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$	2·997 (4)	2·33 (3)	150 (3)
N(1*B*)–H(1*B*)···O(7)	$x-1$,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$	3·302 (4)	2·66 (3)	146 (3)
O(1)–H(11)···O(6*A*)	x,	y,	z	2·704 (3)	1·93 (4)	167 (3)
O(1)–H(12)···O(5)	x,	y,	z	2·676 (4)	1·90 (5)	168 (4)
O(2)–H(21)···O(6*B*)	x,	y,	z	2·688 (4)	2·00 (5)	162 (4)
O(2)–H(22)···O(5)	$\bar{x}$,	$y-\frac{1}{2}$,	$\frac{1}{2}-z$	2·664 (4)	1·86 (5)	176 (3)
O(3)–H(31)···O(6)	$1-x$,	$y-\frac{1}{2}$,	$\frac{1}{2}-z$	2·928 (5)	2·14 (6)	159 (4)
O(3)–H(32)···N(3*A*)	$\bar{x}$,	$\bar{y}$,	$1-z$	3·143 (4)	2·54 (5)	136 (4)
O(4)–H(41)···O(7)	$x-1$,	y,	z	2·870 (5)	2·15 (5)	170 (3)
O(4)–H(42)···N(3*A*)	x,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$	3·089 (4)	2·31 (6)	149 (4)
C(2*A*)–H(2*A*)···O(5)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	3·154 (3)	2·39 (2)	134 (2)

and O(6), O(7). In the corresponding adenine–sulphate complex (Sletten & Thorstensen, 1974) the anion is situated in the coordination sphere and hydrogen-bonded to the amino substituent at C(6). Guanine and hypoxanthine do not have the ability to form a corresponding hydrogen bond to oxyanions, and in order to accommodate hydrogen bonds between purine and anion, an axial metal–anion bond is not established.

Three of the atoms in the sulphate show very large thermal motion (Table 1). A difference map shows residual peaks at O(6), O(7) and O(8) indicating disorder brought about by a rotation around S–O(5) which lies in the pseudo mirror plane. The rotational motion tends to shift the sulphate position from the pseudo mirror-plane-symmetry, where O(6), O(7) are symmetry related, to one where O(8), O(6) or O(8), O(7) are symmetry related. The latter arrangement implies that the H atom at N(1) would be bifurcated.

The molecular packing is shown in Fig. 2. The guanine ligands are stacked on top of each other with an approximately equidistant spacing of 3·34 Å. Other significant intermolecular contacts are between methyl groups. The distances between O(6) and the methyl H atoms are in the range 2·63–2·72 Å for ligand *A* and 2·62–2·89 Å for *B*. Hydrogen-bond distances and angles are given in Table 2. Of the possible hydrogen-bond acceptors on the purines, N(3*B*) is the only one not involved in hydrogen bonding.

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Dipiperidine Disulphide

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Abstract. $C_{10}H_{20}N_2S_2$, monoclinic, $P2_1/c$, $a = 10{\cdot}114$ (8), $b = 11{\cdot}158$ (8), $c = 11{\cdot}390$ (8) Å, $\beta = 96{\cdot}08$ (6)°, $U = 1278$ Å^3, $Z = 4$, $D_x = 1{\cdot}34$ g cm^{-3}, μ(Cu $K\alpha$) = 33·67 cm^{-1}. The structure was solved by direct methods and refined to an R of 0·046 for 1308 unique diffractometer data. The S–S distance is 2·067 Å and N–S–S–N dihedral angle 101·1 (4)°.

Introduction. The structure of dipiperidine disulphide has been determined as part of a study of non-metal sulphides. It was prepared by the action of piperidine on S_2Cl_2 (Michaelis & Luxembourg, 1895) and recrystallized from petroleum spirit. Intensities were determined with a Syntex $P2_1$ four-circle diffractometer, Cu $K\alpha$ radiation, a graphite monochromator and a crystal 0·12 × 0·08 × 0·035 mm. 1603 reflexions were measured; after Lp and numerical absorption corrections, equivalent reflexions were merged to give 1308 reflexions with $F > 2{\cdot}5\sigma(F)$ based on counting statistics. The structure was solved by multisolution Σ_2 sign expansion, and refined by full-matrix least squares with an overall isotropic temperature factor for H and the remaining atoms anisotropic. H coordinates were calculated geometrically and the structure was refined with the constraint that the C–H vectors be constant but the C atoms free to move (C–H 1·08 Å). Complex neutral-atom scattering factors and the weighting scheme $w = 1/[\sigma^2(F) + 0{\cdot}004F^2]$ were employed. The refinement converged to $R' = \Sigma\, w^{1/2}\Delta/\Sigma\, w^{1/2}|F_o| = 0{\cdot}052$ and $R = 0{\cdot}046$. Positional and thermal parameters are presented in Tables 1–3 and the molecular dimensions in Tables 4 and 5.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31995 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

	x	y	z
S(1)	355 (1)	3763 (1)	2807 (1)
S(2)	2238 (1)	3659 (1)	3704 (1)
N(1)	−775 (4)	3009 (3)	3509 (3)
N(2)	3177 (3)	2636 (3)	3083 (3)
C(1)	−1053 (5)	3514 (4)	4633 (5)
C(2)	−2350 (6)	3008 (5)	4982 (5)
C(3)	−2290 (5)	1645 (5)	5036 (5)
C(4)	−1923 (5)	1148 (4)	3891 (5)
C(5)	−632 (5)	1702 (4)	3557 (5)
C(6)	2856 (5)	1367 (4)	3282 (5)
C(7)	4013 (6)	583 (5)	2974 (5)
C(8)	4330 (6)	808 (5)	1726 (5)
C(9)	4576 (5)	2134 (5)	1515 (4)
C(10)	3418 (4)	2879 (4)	1865 (4)

Table 2. *Anisotropic temperature factors* ($\text{Å}^2 \times 10^3$)

The temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^*)$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	55 (1)	50 (1)	80 (1)	15 (1)	20 (1)	1 (1)
S(2)	55 (1)	52 (1)	71 (1)	−12 (1)	14 (1)	−8 (1)
N(1)	50 (2)	41 (2)	71 (3)	−1 (2)	20 (2)	−4 (2)
N(2)	47 (2)	50 (2)	61 (2)	4 (2)	12 (2)	−2 (2)
C(1)	79 (4)	50 (3)	97 (4)	−23 (3)	43 (3)	−11 (3)
C(2)	81 (4)	68 (4)	95 (4)	−20 (3)	47 (3)	−13 (3)
C(3)	57 (4)	71 (4)	86 (4)	11 (3)	19 (3)	−12 (3)
C(4)	69 (4)	46 (3)	101 (4)	−10 (3)	23 (3)	−15 (3)
C(5)	48 (3)	41 (3)	89 (4)	−12 (2)	21 (3)	−7 (2)
C(6)	61 (3)	49 (3)	83 (3)	16 (3)	26 (3)	5 (3)
C(7)	74 (4)	56 (3)	98 (4)	21 (3)	25 (3)	25 (3)
C(8)	66 (4)	61 (3)	89 (4)	2 (3)	25 (3)	17 (3)
C(9)	56 (3)	65 (3)	79 (4)	9 (3)	23 (3)	3 (3)
C(10)	46 (3)	54 (3)	60 (3)	12 (2)	19 (2)	2 (3)

Table 3. *Hydrogen-atom coordinates* ($\times 10^4$)

The U value for each H atom is 0·092 Å^2.

	x	y	z
H(1)	−253	3291	5302
H(1′)	−1135	4476	4554
H(2)	−2517	3352	5840
H(2′)	−3158	3278	4341
H(3)	−3251	1301	5203
H(3′)	−1552	1374	3891
H(4)	−1800	189	3975
H(4′)	−2713	1342	3203
H(5)	−426	1368	2704
H(5′)	176	1465	4212
H(6)	2705	1236	4197
H(6′)	1963	1123	2729
H(7)	3745	−348	3060
H(7′)	4881	780	3579
H(8)	5211	309	1576
H(8′)	3505	510	1117
H(9)	4678	2276	590
H(9′)	5480	2409	2037
H(10)	2535	2660	1287
H(10′)	3646	3818	1776

Table 4. *Bond lengths* (Å)

S(2)–S(1)	2·067 (4)	N(1)–S(1)	1·687 (6)
N(2)–S(2)	1·687 (6)	C(1)–N(1)	1·454 (7)
C(5)–N(1)	1·466 (7)	C(6)–N(2)	1·476 (7)
C(10)–N(2)	1·460 (6)	C(2)–C(1)	1·519 (9)
C(3)–C(2)	1·522 (9)	C(4)–C(3)	1·500 (8)
C(5)–C(4)	1·529 (9)	C(7)–C(6)	1·531 (9)
C(8)–C(7)	1·512 (9)	C(9)–C(8)	1·524 (9)
C(10)–C(9)	1·524 (8)		

Table 5. *Bond angles* (°)

N(1)–S(1)–S(2)	111·9 (2)	N(2)–S(2)–S(1)	111·2 (2)
C(1)–N(1)–S(1)	115·4 (4)	C(5)–N(1)–S(1)	116·4 (4)
C(5)–N(1)–C(1)	112·4 (5)	C(6)–N(2)–S(2)	116·3 (4)
C(10)–N(2)–S(2)	115·5 (4)	C(10)–N(2)–C(6)	112·6 (5)
C(2)–C(1)–N(1)	109·9 (5)	C(3)–C(2)–C(1)	110·5 (5)
C(4)–C(3)–C(2)	110·3 (5)	C(5)–C(4)–C(3)	111·3 (5)
C(4)–C(5)–N(1)	109·1 (5)	C(7)–C(6)–N(2)	109·2 (5)
C(8)–C(7)–C(6)	111·3 (5)	C(9)–C(8)–C(7)	111·4 (5)
C(10)–C(9)–C(8)	110·2 (5)	C(9)–C(10)–N(2)	110·0 (5)

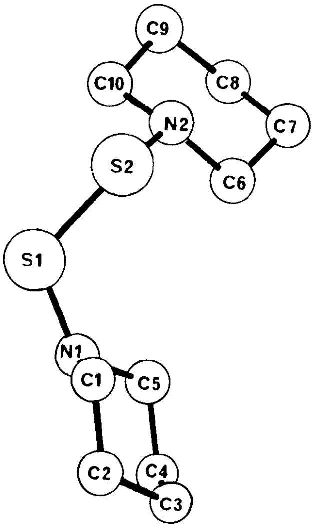

Fig. 1. The molecule of dipiperidine disulphide.

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°) may imply some N—S π 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(1*a*) 2·97; H(3′)···S(1*b*) 2·88 Å; S(1*a*) is generated from S(1) by the symmetry transformation $-x, -\frac{1}{2}+y, \frac{1}{2}-z$ and S(1*b*) 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^{-3}. 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 × 100 × 40 μm 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 $2\theta \leq 60°$, 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^{-1}).

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

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* 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.