

## 1,3-Propanediammonium tetrathio- tungstate and *N,N,N',N'*-tetramethyl- ethylenediammonium tetrathio- tungstate

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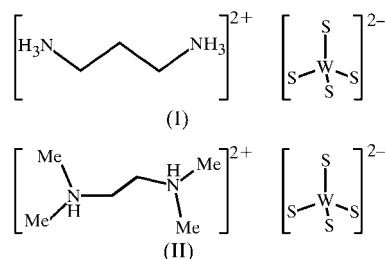
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The title complexes, (C<sub>3</sub>H<sub>12</sub>N<sub>2</sub>)[WS<sub>4</sub>] and (C<sub>6</sub>H<sub>18</sub>N<sub>2</sub>)[WS<sub>4</sub>], contain tetrahedral [WS<sub>4</sub>]<sup>2-</sup> dianions, which accept a complex series of hydrogen bonds from the organic dications. The strength and number of these hydrogen bonds affect the W—S distances.

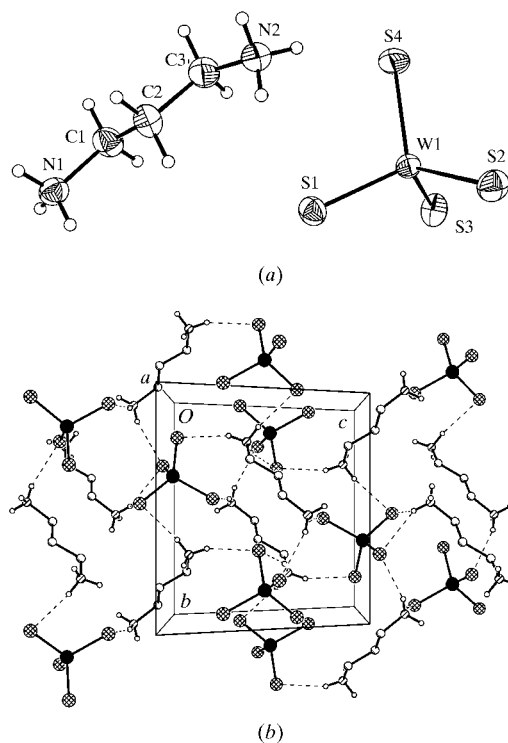
### Comment

Sulfur complexes of the group VI metals Mo (Coucouvanis, 1998) and W (Shibahara, 1993) are a unique class of compounds encompassing an unusually wide range of metal–sulfur stoichiometries, metal oxidation states, coordination geometries and bonding modes of the sulfide ligands. The tetrahedral [MS<sub>4</sub>]<sup>2-</sup> (*M* = Mo or W) complexes are routinely used as starting materials for the preparation of a variety of structurally diverse di-, tri- and tetranuclear metal–sulfur complexes. The flexibility of the [MS<sub>4</sub>]<sup>2-</sup> unit is evidenced by its occurrence in different structural environments, as seen in the complexes [Ni(en)<sub>3</sub>][MoS<sub>4</sub>] (*en* is 1,2-diaminoethane; Ellermeier *et al.*, 1999*a*), [Co<sub>2</sub>(tren)<sub>3</sub>][MoS<sub>4</sub>]<sub>2</sub> [*tren* is tris(2-aminoethyl)amine; Ellermeier & Bensch, 2001*a*], [Mn(dien)<sub>2</sub>][MoS<sub>4</sub>] (*dien* is diethylenetriamine; Ellermeier & Bensch, 2002), [Ni(tren)<sub>2</sub>][WS<sub>4</sub>] (Ellermeier *et al.*, 2002), [W(WS<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> (Bhaduri & Ibers, 1986), [SW(WS<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> (Muller *et al.*, 1981, and references therein), [(W<sub>2</sub>S<sub>4</sub>)(WS<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> (Secheresse *et al.*, 1982) and [Ni(WS<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> (Muller & Diemann, 1971). The reactivity of [MS<sub>4</sub>]<sup>2-</sup> towards several organic substrates, such as dibenzyl trisulfide (Simhon *et al.*, 1981), diphenyl disulfide (Pan *et al.*, 1984), 1,1-dithiolate disulfide (McConnachie & Stiefel, 1999) and alkyl halides (Dhar & Chandrasekaran, 1989), has been investigated. However, the reactions of [MS<sub>4</sub>]<sup>2-</sup> with organic amines have not been studied in detail (Srinivasan *et al.*, 2001). These investigations are especially

important in view of the accessibility of novel metal–sulfide complexes under mild solvothermal conditions using organic amines (Ellermeier *et al.*, 1999*b*, 2002; Ellermeier & Bensch, 2001*b*, 2002). In addition, it was reported that piperidinium tetrathiotungstate (Dhar & Chandrasekaran, 1989) and benzyltriethylammonium tetrathiomolybdate can be used as sulfur-transfer reagents in organic synthesis for the formation of novel organo–sulfur compounds under mild reaction conditions (Prabhu *et al.*, 2000). In continuation of our recent



report on the structure determination of (enH<sub>2</sub>)[WS<sub>4</sub>] (Srinivasan *et al.*, 2002), we have structurally characterized two new [WS<sub>4</sub>]<sup>2-</sup> complexes by reacting (NH<sub>4</sub>)<sub>2</sub>[WS<sub>4</sub>] with two different diamines. The two amines, 1,3-propanediamine (1,3-pn) and *N,N,N',N'*-tetramethylethylenediamine (*tmen*), have different steric bulk and different numbers of potential hydrogen-bonding donors. Both diamines readily afford the corresponding organic diammonium salts of [WS<sub>4</sub>]<sup>2-</sup>, *viz.* (I) and (II), respectively, in good yields.

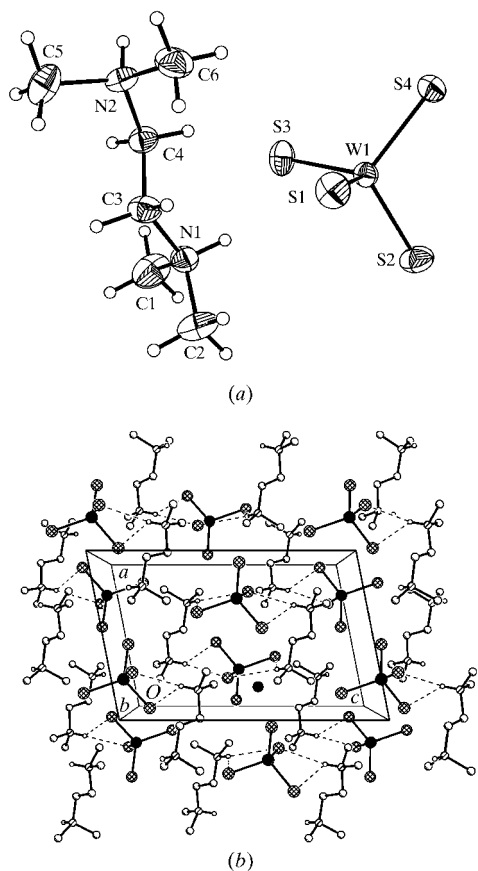


**Figure 1**  
(*a*) A view of (I) showing the atom labelling and displacement ellipsoids at the 50% probability level. (*b*) The crystal packing viewed along the *a* axis. Dashed lines indicate hydrogen bonding.

Compound (I) contains discrete  $(1,3\text{-pnH}_2)^{2+}$  dications and  $[\text{WS}_4]^{2-}$  anions (Fig. 1). The  $\text{WS}_4$  tetrahedron is very slightly distorted, with  $\text{S}-\text{W}-\text{S}$  angles ranging between  $108.04$  (5) and  $110.37$  (5) $^\circ$ . The  $\text{W}-\text{S}$  bond lengths range from  $2.1798$  (12) to  $2.1946$  (10) Å (Table 1). All structural parameters of (I) are in good agreement with those reported for  $(\text{enH}_2)[\text{WS}_4]$ . Taking into account the s.u. values, the  $\text{W}-\text{S}$  bond distances in (I) are in the range reported for  $(\text{NH}_4)_2[\text{WS}_4]$  (Lapasset *et al.*, 1976). The cation and anion are connected *via* hydrogen bonding. The differing  $\text{W}-\text{S}$  bond distances may be due to the different numbers and strengths of hydrogen-bonding contacts between the H atoms attached to the N atoms of the cation and the S atoms. Seven short intermolecular  $\text{S}\cdots\text{H}$  contacts are observed, with  $\text{N}\cdots\text{S}$  distances ranging from  $3.277$  (4) to  $3.458$  (4) Å and  $\text{N}-\text{H}\cdots\text{S}$  angles ranging from  $124$  to  $169^\circ$  (Fig. 1 and Table 2). Atom S3 has one short contact, while the other S atoms have two short contacts each. The  $\text{W}-\text{S}$  bond lengths tend to be longer when the  $\text{S}\cdots\text{H}$  contacts are shorter and the  $\text{N}-\text{H}\cdots\text{S}$  angles are more linear (Table 2).

Compound (II) is composed of discrete  $[\text{WS}_4]^{2-}$  anions and  $(\text{tmenH}_2)^{2+}$  cations (Fig. 2). The  $\text{S}-\text{W}-\text{S}$  bond angles are nearly identical, with values ranging from  $109.13$  (5) to

$109.85$  (6) $^\circ$ , while the  $\text{W}-\text{S}$  bond lengths vary from  $2.1772$  (13) to  $2.1995$  (13) Å (Table 3). These structural parameters are in good agreement with those reported for the above-mentioned complexes and those observed in (I). Considering the s.u. values, the  $\text{W}-\text{S3}$  distance of  $2.1995$  (13) Å is in agreement with the longest  $\text{W}-\text{S}$  distance of  $2.1946$  (10) Å found in (I). In view of the lower number of donor H atoms in (II) compared with (I), only four short intermolecular  $\text{N}-\text{H}\cdots\text{S}$  contacts are observed (Table 4). Atom S3 is involved in two short contacts, while atoms S1 and S4 have only one such contact. This feature is responsible for the presence of the short  $\text{W}-\text{S2}$  bond distance of  $2.1771$  (13) Å and the long  $\text{W}-\text{S3}$  bond distance of  $2.1995$  (13) Å. Note that for  $[\text{Ni}(\text{tren})_2][\text{WS}_4]$  (Ellermeier *et al.*, 2002), which has an extended hydrogen-bond network, a very short  $\text{W}-\text{S}$  bond of  $2.1580$  (10) Å and a long bond of  $2.212$  (9) Å were reported. The  $\text{N}-\text{H}\cdots\text{S}$  angles in (II) range from  $131$  to  $143^\circ$  (Table 4 and Fig. 2). Because (I) and (II) contain different numbers of hydrogen bonds, different crystal packings are generated, *viz.* a three-dimensional network in (I) and isolated groups consisting of two cations and two anions in (II) (compare Figs. 1 and 2). Further studies employing differently substituted amines are in progress in order to understand the influence of the alkyl groups attached to the N atom of the amine on the  $\text{W}-\text{S}$  bond distances.



**Figure 2**  
(a) A view of (II) showing the atom labelling and displacement ellipsoids drawn at the 50% probability level. (b) The crystal packing viewed along the crystallographic  $b$  axis. Dashed lines indicate hydrogen bonding.

## Experimental

$(\text{NH}_4)_2[\text{WS}_4]$  (348 mg, 1 mmol) was dissolved in distilled water (10 ml) and the solution was filtered. The organic diamine 1,3-pn (0.3 ml) was added to the clear yellow filtrate and the reaction mixture was left undisturbed in a 100 ml glass beaker in a refrigerator. After a day, well formed crystals of (I) separated. The crystals were filtered off, washed with cold water (5 ml), followed by 2-propanol (5 ml) and diethyl ether (99 ml), and air-dried. The yield was 65%. The use of tmen (0.4 ml) instead of 1,3-pn in the above synthesis resulted in the formation of (II), in a 60% yield. Both complexes are stable in air.

## Compound (I)

### Crystal data

$(\text{C}_3\text{H}_{12}\text{N}_2)[\text{WS}_4]$   
 $M_r = 388.24$   
Monoclinic,  $P2_1/c$   
 $a = 10.801$  (2) Å  
 $b = 10.609$  (2) Å  
 $c = 10.774$  (2) Å  
 $\beta = 119.60$  (3) $^\circ$   
 $V = 1073.5$  (5) Å<sup>3</sup>  
 $Z = 4$

$D_x = 2.402$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 94 reflections  
 $\theta = 15.5\text{--}19^\circ$   
 $\mu = 11.48$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
Block, yellow  
 $0.11 \times 0.10 \times 0.08$  mm

### Data collection

Stoe AED-II four-circle diffractometer  
 $\omega$ - $\theta$  scans  
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)  
 $T_{\text{min}} = 0.291$ ,  $T_{\text{max}} = 0.401$   
4124 measured reflections  
3126 independent reflections  
2663 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$   
 $\theta_{\text{max}} = 30.0^\circ$   
 $h = -15 \rightarrow 13$   
 $k = -2 \rightarrow 14$   
 $l = -1 \rightarrow 15$   
4 standard reflections  
frequency: 120 min  
intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.024$   
 $wR(F^2) = 0.061$   
 $S = 1.04$   
 3126 reflections  
 94 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 0.5352P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.54 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -1.84 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0024 (2)

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I).

W1–S3	2.1798 (12)	N1–C1	1.492 (5)
W1–S4	2.1931 (12)	C1–C2	1.508 (6)
W1–S2	2.1936 (10)	C2–C3	1.517 (6)
W1–S1	2.1946 (10)	C3–N2	1.485 (6)
S3–W1–S4	110.22 (6)	S2–W1–S1	109.57 (4)
S3–W1–S2	109.26 (4)	N1–C1–C2	110.4 (3)
S4–W1–S2	110.37 (5)	C1–C2–C3	111.2 (4)
S3–W1–S1	108.04 (5)	N2–C3–C2	111.0 (4)
S4–W1–S1	109.33 (5)		

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1N1 $\cdots$ S1 <sup>i</sup>	0.89	2.44	3.284 (3)	158
N1–H2N1 $\cdots$ S1 <sup>ii</sup>	0.89	2.43	3.277 (4)	159
N1–H3N1 $\cdots$ S2 <sup>iii</sup>	0.89	2.53	3.407 (4)	169
N2–H1N2 $\cdots$ S4 <sup>iv</sup>	0.89	2.58	3.357 (4)	146
N2–H1N2 $\cdots$ S2 <sup>iv</sup>	0.89	2.81	3.394 (4)	124
N2–H2N2 $\cdots$ S4	0.89	2.61	3.458 (4)	160
N2–H3N2 $\cdots$ S3 <sup>v</sup>	0.89	2.47	3.335 (4)	163

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

## Compound (II)

### Crystal data

$(\text{C}_6\text{H}_{18}\text{N}_2)[\text{WS}_4]$   
 $M_r = 430.31$   
 Monoclinic,  $P2_1/n$   
 $a = 8.5916$  (11)  $\text{\AA}$   
 $b = 12.3365$  (10)  $\text{\AA}$   
 $c = 13.3799$  (9)  $\text{\AA}$   
 $\beta = 101.113$  (8)  $^\circ$   
 $V = 1391.5$  (2)  $\text{\AA}^3$   
 $Z = 4$   
 $D_x = 2.054$   $\text{Mg m}^{-3}$

### Data collection

Phillips PW1100 four-circle diffractometer  
 $\omega$ - $\theta$  scans  
 Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)  
 $T_{\min} = 0.390$ ,  $T_{\max} = 0.541$   
 4851 measured reflections  
 3363 independent reflections  
 2725 reflections with  $I > 2\sigma(I)$

Mo  $K\alpha$  radiation  
 Cell parameters from 116 reflections  
 $\theta = 15$ – $18.5^\circ$   
 $\mu = 8.87$   $\text{mm}^{-1}$   
 $T = 293$  (2) K  
 Block, orange  
 $0.14 \times 0.09 \times 0.07$  mm

$R_{\text{int}} = 0.040$   
 $\theta_{\text{max}} = 28.0^\circ$   
 $h = -1 \rightarrow 11$   
 $k = -16 \rightarrow 3$   
 $l = -17 \rightarrow 17$   
 4 standard reflections  
 frequency: 120 min  
 intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.069$   
 $S = 1.07$   
 3363 reflections  
 119 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0323P)^2 + 1.5856P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.99 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -2.09 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0064 (3)

**Table 3**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II).

W1–S2	2.1772 (13)	C2–N1	1.490 (6)
W1–S1	2.1864 (13)	N1–C3	1.502 (6)
W1–S4	2.1932 (13)	C3–C4	1.516 (6)
W1–S3	2.1995 (13)	N2–C6	1.487 (6)
C1–N1	1.485 (7)	N2–C5	1.492 (7)
S2–W1–S1	109.77 (5)	C1–N1–C3	112.9 (4)
S2–W1–S4	109.49 (5)	C2–N1–C3	110.1 (4)
S1–W1–S4	109.14 (5)	N1–C3–C4	110.9 (4)
S2–W1–S3	109.85 (6)	N2–C4–C3	112.1 (4)
S1–W1–S3	109.45 (5)	C6–N2–C5	111.7 (4)
S4–W1–S3	109.13 (5)	C6–N2–C4	113.4 (4)
C1–N1–C2	110.9 (5)	C5–N2–C4	112.9 (4)

**Table 4**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1N1 $\cdots$ S1	0.91	2.72	3.387 (4)	131
N1–H1N1 $\cdots$ S3	0.91	2.80	3.570 (4)	143
N2–H1N2 $\cdots$ S4 <sup>i</sup>	0.91	2.56	3.266 (4)	135
N2–H1N2 $\cdots$ S3 <sup>i</sup>	0.91	2.79	3.533 (4)	140

Symmetry code: (i)  $1-x, 1-y, 1-z$ .

The H atoms bound to C atoms in each structure, and the H atoms bound to N atoms in (II), were positioned with idealized geometry ( $C-H = 0.96$ – $0.97$   $\text{\AA}$  and  $N-H = 0.91$   $\text{\AA}$ ) and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for the methyl H atoms and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$  for the other H atoms. The positions of the N–H H atoms of (I) were idealized with N–H distances of 0.89  $\text{\AA}$  and then refined as rigid groups, which were allowed to rotate but not tip, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$ . The largest peak in the residual electron-density map for (I) is 0.84  $\text{\AA}$  from W1.

For both compounds, data collection: *DIF4* (Stoe & Cie, 1998); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1158). Services for accessing these data are described at the back of the journal.

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