

Competing hydrogen-bond acceptors in ethylenediammonium oxotrithio-tungstate(VI)

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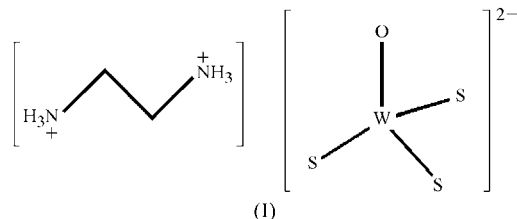
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The structure of the title compound, (C₂H₁₀N₂)[WOS₃], consists of ethylenediammonium dication and tetrahedral [WOS₃]²⁻ dianions, which are linked with the aid of four varieties of hydrogen bond, namely N—H···O, N—H···S, C—H···O and C—H···S. The strength and number of these hydrogen bonds affect the W—O and W—S bond distances.

Comment

As part of an ongoing research programme, we are investigating the reactions of (NH₄)₂[WS₄] with organic amines and have structurally characterized several organic ammonium tetrathiotungstates (Srinivasan *et al.*, 2002, 2003*a,b*, 2005, 2006, 2006*a,b*). Our recent results in this area have revealed that these compounds exhibit a rich structural chemistry in terms of the N—H···S interactions between the organic ammonium cation and the tetrathiotungstate anion (Srinivasan, Näther *et al.*, 2006*a,b*). In almost all these compounds, the WS₄ tetrahedron is slightly distorted, with one or two of the W—S bonds elongated, which can be attributed to the strength and number of these S···H interactions. A competing hydrogen-bond acceptor, such as oxygen in oxotrithiotungstate [WOS₃]²⁻ compounds, offers the possibility to investigate the occurrence of N—H···O as well as N—H···S interactions in the same compound. Although the synthetic aspects of [WOS₃]²⁻ (Müller & Diemann, 1968; McDonald *et al.*, 1983), spectral characteristics (Müller *et al.*, 1969, 1981), reactivity studies (Ansari *et al.*, 1988) and medical applications (Mason *et al.*, 1989) have been reported in the literature, only two structurally characterized monooxotrithiotungstates, namely K₃[WOS₃]Cl (Krebs *et al.*, 1972) and (pipH)₄[WOS₃][WS₄] (pipH is piperidinium) (Siemeling *et al.*, 2006), are known to date. Both reported compounds are double salts and contain Cl⁻ or [WS₄]²⁻ anions in addition to [WOS₃]²⁻ in their structures. In the present work, we describe the structure of

the organic ammonium oxotrithiotungstate (enH₂)[WOS₃] (enH₂ is ethylenediammonium), (I), which does not contain any anion other than [WOS₃]²⁻. The title compound was prepared by following a procedure analogous to that used previously for the corresponding tetrathio compound (enH₂)[WS₄] (Srinivasan *et al.*, 2002).



The structure of (I) consists of ethylenediammonium dication and tetrahedral [WOS₃]²⁻ dianions, with all atoms located in general positions (Fig. 1). Both (pipH)₂[WS₄] and the double salt (pipH)₄[WOS₃][WS₄] crystallize in the monoclinic space group *P*2₁/*n* (Siemeling *et al.*, 2006), while the tetrathio analogue of (I), *viz.* (enH₂)[WS₄], crystallizes in the chiral orthorhombic space group *P*2₁2₁2₁ (Srinivasan *et al.*, 2002). The geometric parameters of the (enH₂)²⁺ cation in (I) (Table 1) are in good agreement with those observed in other compounds containing the same cation (Srinivasan *et al.*, 2002, 2003*c*). The bond angles around the W atom are very close to the ideal tetrahedral angle and scatter in a small range between 108.63 (14) and 110.36 (6)°. The observed W—O and W—S bond distances are in very good agreement with those reported in the double salt (pipH)₄[WOS₃][WS₄] (Siemeling *et al.*, 2006). Analysis of the crystal structure showed the presence of four varieties of weak interactions, namely N—H···O, N—H···S, C—H···O and C—H···S bonds. Each cation is hydrogen bonded to six different [WOS₃]²⁻ anions. The S and O atoms of [WOS₃]²⁻ function as H-atom acceptors, while the cation acts as a H-atom donor through its ammonium and methylene groups. Each anion is linked to six different cations with the aid of the same four varieties of hydrogen bonds (Fig. 2). In (I), all H atoms involved in hydrogen bonding are singly shared donors, except for H1N1, which functions as a bifurcated donor. As a result of the hydrogen-bonding pattern, the cations and anions are organized into alternating layers, leading to the formation of a three-dimensional hydrogen-bonded network (Fig. 3).

A total of nine hydrogen bonds (Table 2) comprising six S···H and three O···H interactions are observed, and all

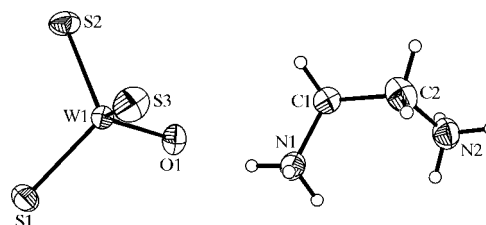


Figure 1

The structure of the constituent ions of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

these contacts are shorter than the sum of their van der Waals radii (Bondi, 1964). A comparison of the geometric parameters of (I) with those of $K_3[WOS_3]Cl$ and $(pipH)_4[WOS_3][WS_4]$ (Table 3) serves to illustrate the importance of hydrogen bonding in organic ammonium thiotungstates. In $K_3[WOS_3]Cl$, with no hydrogen bonding, the W—S distances scatter in a narrow range between 2.196 (6) and 2.208 (5) Å. The difference, Δ , between the longest and shortest W—S bonds is 0.012 Å, which is much less than the values in (I) and $(pipH)_4[WOS_3][WS_4]$, with a maximum Δ value of 0.0399 Å. It should be noted that the structure of $(pipH)_4[WOS_3][WS_4]$ was determined at 220 K and the compound also contains an additional $[WS_4]^{2-}$ anion in its structure. In (I), the shortest W—S bond length of 2.1791 (15) Å is observed for S3, which is involved in a single bifurcated $S \cdots H$ contact at a relatively long distance of 2.77 Å accompanied by a small $N-H \cdots S$ angle, which can explain the observed short W—S distance. In $(pipH)_4[WOS_3][WS_4]$, the shortest W—S bond of 2.1666 (9) Å was explained as being due to the absence of any short $S \cdots H$ contact. The other two W—S bond distances in (I), at 2.2010 (14) and 2.2029 (14) Å, are identical within experimental error. Atom S2 is engaged in two short $N-H \cdots S$ contacts, while S1 has three hydrogen-bonding interactions (two short $N-H \cdots S$ and one $C-H \cdots S$ contact), which can explain the elongation of these bonds compared to W—S3. The observation of longer W—S bonds at 2.2009 (10) and 2.2065 (10) Å in $(pipH)_4[WOS_3][WS_4]$ was attributed to a singly shared hydrogen bond involving each of these S atoms.

The W—O bond distance in (I) [1.778 (4) Å] is slightly longer than that for $K_3[WOS_3]Cl$ [1.76 (1) Å]. An elongation

of the W—O bond with respect to related compounds, which do not exhibit $O \cdots H$ contacts, is indicated by the observed W—O stretching vibration in the IR spectrum of (I), which occurs as a strong signal centred at 828 cm^{-1} . For the fully alkylated organic ammonium compound $[(C_2H_5)_4N]_2[WOS_3]$ (McDonald *et al.*, 1983) and the pure inorganic $Cs_2[WOS_3]$ (Müller *et al.*, 1969) the W—O vibrational frequencies are at higher energies of 885 and 870 cm^{-1} , respectively. A value of 793 cm^{-1} was found in $(pipH)_4[WOS_3][WS_4]$ (Siemeling *et al.*, 2006). In this double salt, the $N-H \cdots O$ contacts are slightly shorter (1.89 and 1.93 Å) and are accompanied by larger $D-H \cdots A$ angles (170 and 173°) than those observed in (I). Although the W—O distances of (I) and $(pipH)_4[WOS_3][WS_4]$ are nearly the same, it is to be noted that the O atom in (I) is involved in three hydrogen bonds, which includes two singly shared $N-H \cdots O$ interactions and a singly shared $C-H \cdots O$ contact.

The occurrence of $C-H \cdots O$ and $C-H \cdots S$ contacts of 2.57 and 2.88 Å, respectively, in (I) prompted us to reinvestigate the known structures of $(enH_2)[WS_4]$ and $(pipH)_4[WOS_3][WS_4]$ for the presence of additional weak interactions. Scrutiny of the structure of $(enH_2)[WS_4]$ revealed that, in addition to the reported $N-H \cdots S$ bonds, the $[WS_4]^{2-}$ unit is involved in three weak $C-H \cdots S$ contacts of 2.89, 2.92 and 2.95 Å, with corresponding $D-H \cdots A$ angles of 148, 131 and 143° . In $(pipH)_4[WOS_3][WS_4]$, the $[WOS_3]^{2-}$ unit exhibits three weak $C-H \cdots S$ contacts of 2.87, 2.93 and 2.96 Å, with corresponding $D-H \cdots A$ angles of 127, 133 and 156° . The $C-H \cdots O$ distance of 2.76 Å seems to be too long for significant interaction (Jeffrey, 1997). Presently, there is no direct evidence to show that $C-H \cdots S$ bonds affect the W—S bond distances. However, the observation of several $C-H \cdots S$ contacts in many tetrathiotungstates by us recently (Srinivasan *et al.*, 2006, 2007) indicates that these weak interactions may play an important role in the structural chemistry of thiotungstates.

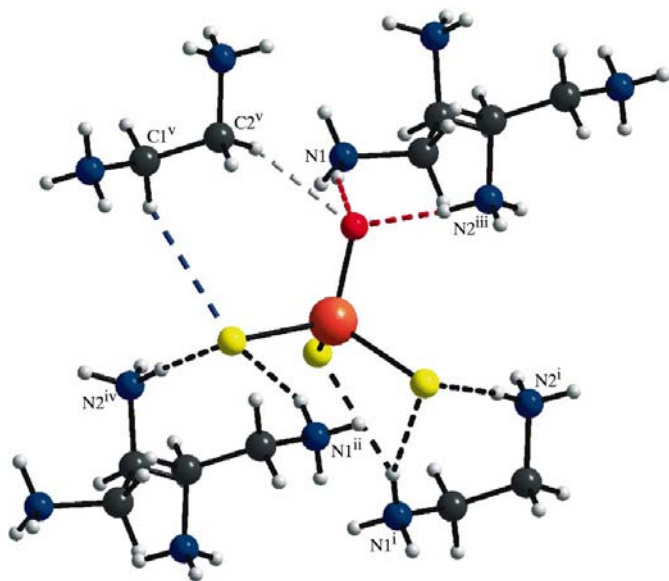


Figure 2

A view of the environment of the $[WOS_3]^{2-}$ anion, showing the linking of each anion to six different cations via $N-H \cdots O$, $N-H \cdots S$, $C-H \cdots O$ and $C-H \cdots S$ interactions. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x + 1, y, z$; (v) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$]

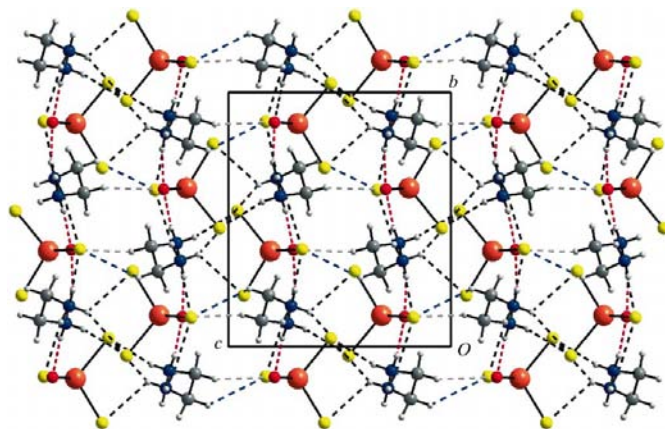
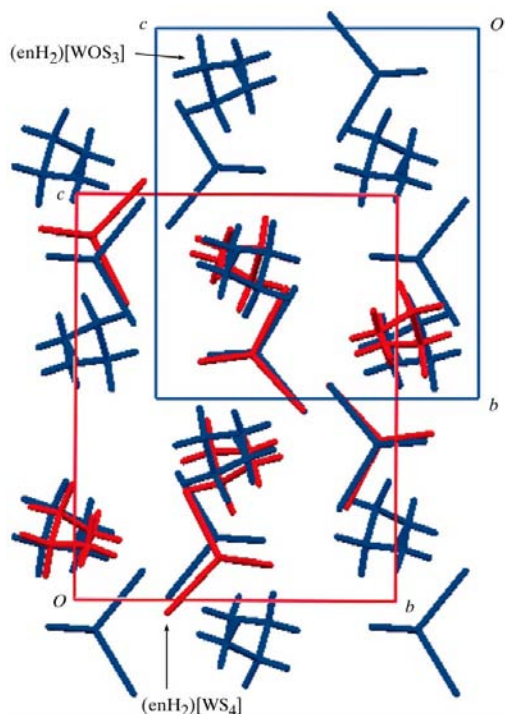


Figure 3

The packing of (I), viewed along the a axis, showing the three-dimensional hydrogen-bond network. $N-H \cdots O$, $N-H \cdots S$, $C-H \cdots O$ and $C-H \cdots S$ interactions are shown as dashed lines.


Figure 4

An overlay diagram showing the structural similarity of $(\text{enH}_2)[\text{WOS}_3]$ (blue in the electronic version of the paper) and $(\text{enH}_2)[\text{WS}_4]$ (red).

A comparison of (I) with that of the corresponding tetrathio compound $(\text{enH}_2)[\text{WS}_4]$ reveals that the two structures are nearly identical (Fig. 4). A careful analysis of the overlaid structures demonstrates that when one S atom in $(\text{enH}_2)[\text{WS}_4]$ is replaced by an O atom, the O atom occupies the position of that S atom in $(\text{enH}_2)[\text{WS}_4]$ (Table 3), which exhibits two singly shared N—H \cdots S contacts. It is to be noted that in $(\text{enH}_2)[\text{WS}_4]$ the other three S atoms are involved in at least one bifurcated N—H \cdots S bond. Hence, the preference of this position by the O atom can be explained as due to its competing to engage in stronger hydrogen bonding. The incorporation of oxygen also results in a C—H \cdots O contact. In the tetrathio compound this bond corresponds to the weak C—H \cdots S interaction of 2.89 Å. The structural similarity of the tetrathio and oxotrithio compounds can also explain the similar hydrogen-bond environments of the S atoms that exhibit the longest W—S bond distances in the two compounds. It is interesting that the introduction of an O atom in place of one S atom in the tetrathio compound results in about a two and a half times increase in the magnitude of Δ from 0.0092 Å in $(\text{enH}_2)[\text{WS}_4]$ to 0.0238 Å in (I). This observation adds more credence to our recent postulation that the magnitude of Δ can be considered as a useful measure of the distortion of the WS_4 tetrahedron in organic ammonium oxotrithiotungstates (Srinivasan *et al.*, 2006a).

In summary, we have shown that when an S atom in $(\text{enH}_2)[\text{WS}_4]$ is replaced by an O atom, the resulting structure is nearly identical to that of the tetrathio compound, with the O atom occupying a position favourable for stronger N—

H \cdots O interactions. The O-atom substitution is also accompanied by a pronounced increase in the Δ value for the oxotrithio compound. In addition, the introduction of asymmetry in the form of an O atom in the WS_4 tetrahedron leads to the observation of more varieties of hydrogen bonds in a single compound. More examples of structurally characterized organic ammonium oxotrithiotungstates are essential for a better understanding of the importance of the weaker C—H \cdots O and C—H \cdots S interactions in the structural chemistry of oxotrithiotungstates. Efforts in this direction are currently underway in our laboratories.

Experimental

$(\text{NH}_4)_2[\text{WOS}_3]$ (664 mg, 2 mmol) was dissolved in water (10 ml) containing a few drops of aqueous ammonia and the solution filtered. To the clear yellow filtrate, ethylenediamine (0.3 ml) was added dropwise at room temperature and the reaction mixture was kept aside for crystallization. After a day, crystalline blocks started to separate out slowly. These were isolated by filtration, washed well with ice-cold water (2 ml), 2-propanol (20 ml) and ether (20 ml), and air dried (yield 500 mg). The complex is quite stable in air and was analyzed satisfactorily. IR: $\nu_{\text{W-O}} = 828 \text{ cm}^{-1}$, $\nu_{\text{W-S}} = 484$ and 455 cm^{-1} .

Crystal data

$(\text{C}_2\text{H}_{10}\text{N}_2)[\text{WOS}_3]$
 $M_r = 358.15$
 Monoclinic, $P2_1/n$
 $a = 8.8191$ (14) Å
 $b = 10.7923$ (18) Å
 $c = 9.3793$ (14) Å
 $\beta = 90.631$ (12) $^\circ$
 $V = 892.7$ (2) Å 3

$Z = 4$
 $D_x = 2.665 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 13.58 \text{ mm}^{-1}$
 $T = 293$ (2) K
 Block, yellow
 $0.19 \times 0.18 \times 0.17 \text{ mm}$

Data collection

Stoe AED-II four-circle diffractometer
 ω/θ scans
 Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)
 $T_{\text{min}} = 0.091$, $T_{\text{max}} = 0.135$
 3022 measured reflections

2602 independent reflections
 2052 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 30.0^\circ$
 4 standard reflections
 frequency: every 120 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.070$
 $S = 1.08$
 2602 reflections
 85 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + 2.4809P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.79 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -2.13 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0020 (2)

Table 1

Selected geometric parameters (Å, $^\circ$).

W1—O1	1.778 (4)	N1—C1	1.487 (7)
W1—S3	2.1791 (15)	N2—C2	1.479 (8)
W1—S1	2.2010 (14)	C1—C2	1.508 (9)
W1—S2	2.2029 (14)		
O1—W1—S3	108.63 (14)	S3—W1—S2	109.96 (6)
O1—W1—S1	109.15 (14)	S1—W1—S2	110.36 (6)
S3—W1—S1	109.75 (7)	N1—C1—C2	113.5 (5)
O1—W1—S2	108.95 (15)	N2—C2—C1	112.2 (5)

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N1...S2 ⁱ	0.89	2.68	3.496 (5)	153
N1—H1N1...S3 ⁱ	0.89	2.77	3.353 (5)	125
N1—H2N1...O1	0.89	1.94	2.801 (6)	163
N1—H3N1...S1 ⁱⁱ	0.89	2.47	3.317 (5)	159
N2—H1N2...S2 ⁱ	0.89	2.50	3.375 (6)	168
N2—H2N2...O1 ⁱⁱⁱ	0.89	1.95	2.816 (7)	165
N2—H3N2...S1 ^{iv}	0.89	2.48	3.356 (6)	167
C1—H1A...S1 ^v	0.97	2.88	3.666 (6)	138
C2—H2A...O1 ^v	0.97	2.57	3.474 (8)	155

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

Table 3
Comparative geometric parameters (Å) for K₃[WOS₃]Cl (*A*), (pipH)₄[WOS₃][WS₄] (*B*), (enH₂)[WOS₃] (*C*) and (enH₂)[WS₄] (*D*).

Parameter	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
W—O/S	1.76 (1)	1.776 (2)	1.778 (4)	2.1927 (14)
W—S	2.196 (6)	2.1666 (9)	2.1791 (15)	2.1852 (13)
W—S	2.197 (6)	2.2009 (10)	2.2010 (14)	2.1851 (14)
W—S	2.208 (5)	2.2065 (10)	2.2029 (14)	2.1943 (13)
Δ	0.012	0.0399	0.0238	0.0092

Notes: (*A*) Krebs *et al.* (1972); (*B*) Siemeling *et al.* (2006), pipH is piperidinium; (*C*) this work; (*D*) Srinivasan *et al.* (2002), enH₂ is ethylenediammonium.

All H atoms were located in a difference map; their bond lengths were set to ideal values and H-atom parameters were refined using a riding model (C—H = 0.97 Å and N—H = 0.89 Å). The largest peak in the residual electron-density map is located 0.78 Å from atom W1 and the deepest hole is located 0.79 Å also from W1.

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: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *CIFTAB* in *SHELXTL* (Bruker, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3050). Services for accessing these data are described at the back of the journal.

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