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Diammonium tetrathiotungstate(VI), $(NH_4)_2[WS_4]$, at 150 K

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(W–S) = 0.001 Å
R factor = 0.018
wR factor = 0.048
Data-to-parameter ratio = 25.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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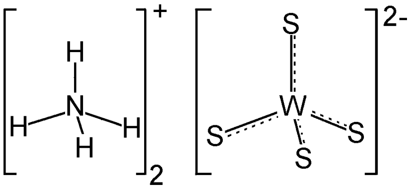
A low-temperature structure determination of the title compound, $(NH_4)_2[WS_4]$, indicates several short N—H···S contacts between the two crystallographically independent ammonium cations and the tetrahedral $[WS_4]^{2-}$ anions, which are all located on crystallographic mirror planes.

Comment

In recent work, it has been shown that the $(NH_4)^+$ ion significantly influences the chemical behaviour of $[MoS_4]^{2-}$; this has been attributed to hydrogen-bonding interactions between the cations and anions in $(NH_4)_2[MoS_4]$ (Schwarz *et al.*, 2003). In view of our recent interest in the chemistry of tetrathiotungstates (Srinivasan *et al.*, 2003), we have redetermined the structure of diammonium tetrathiotungstate at low temperature. The title compound, (I), is isostructural with $(NH_4)_2[MoS_4]$ (Lapasset *et al.*, 1976), $Cs_2[MoS_4]$ (Raymond *et al.*, 1995), $Rb_2[MoS_4]$ (Ellermeier *et al.*, 1999), $K_2[MoS_4]$ (Emirdag-Eanes & Ibers, 2001) and $Rb_2[WS_4]$ (Yao & Ibers, 2004). The cell constants and space group for (I) are consistent with earlier results determined from oscillation photographs (Sasvári, 1963). In contrast with the older work, we have located the H atoms.



(I)

The asymmetric unit of (I) consists of halves of a tetrahedral $[WS_4]^{2-}$ ion and two crystallographically independent ammonium cations, which are all located on crystallographic mirror planes (Fig. 1). The W—S distances range from 2.1856 (11) to 2.2090 (10) Å (Table 1) and are comparable with those of 2.171 (2)–2.205 (2) Å recently reported for $Rb_2[WS_4]$ (Yao & Ibers, 2004). In the crystal structure, anions and cations are linked *via* N—H···S hydrogen bonding (Fig. 2). No disordering of the H atoms in the NH_4^+ ion is found in (I), unlike in the corresponding Mo analogue, where the H atoms are disordered over two orientations of both NH_4^+ cations (Schwarz *et al.*, 2003). Several short N—H···S contacts, with H···S ranging from 2.57 to 3.03 Å, are observed between the cations and the anions, which are comparable with those of 2.55–3.02 Å reported for the Mo analogue (Table 2). The N···S distances for one of the cations fall in the

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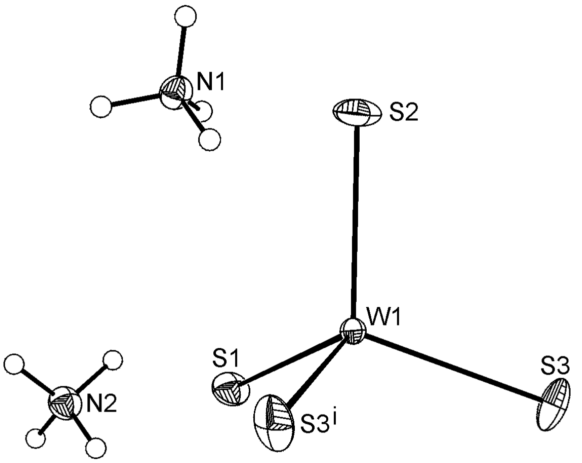

Figure 1
The constituent ions of diammonium tetrathiotungstate, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level [symmetry code: (i) $x, \frac{3}{2} - y, z$].

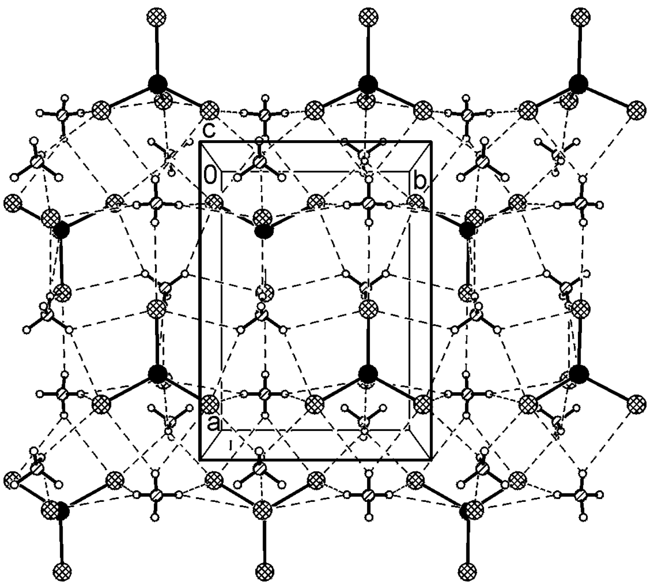

Figure 2
The crystal structure of diammonium tetrathiotungstate, viewed along the c axis (intermolecular hydrogen bonds are shown as dashed lines). Key: W atoms are black circles, S atoms crosshatched circles and N atoms circles shaded bottom left to top right.

range 3.242 (4)–3.5552 (7) Å, while the N···S distances for the second cation are longer, at 3.483 (4)–3.633 (4) Å (Table 2).

Experimental

The title complex was prepared according to the procedure reported by McDonald *et al.* (1983). The product was obtained as orange–yellow crystalline blocks in 60% yield by passing a rapid stream of H_2S gas for 9 h at 333 K into a solution of tungstic acid (5 g) dissolved in concentrated ammonium hydroxide (40 ml) and water (10 ml). At the end of 9 h, the reaction mixture was filtered and the filtrate was set aside for a day, resulting in the formation of crystals of the title complex.

Crystal data

$(NH_4)_2[WS_4]$
$M_r = 348.17$
Orthorhombic, *Pnma*
$a = 9.6054$ (6) Å
$b = 6.9863$ (5) Å
$c = 12.2557$ (10) Å
$V = 822.43$ (10) Å^3
$Z = 4$
$D_x = 2.812$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7250 reflections
$\theta = 10$–25°
$\mu = 14.97$ mm^{-1}
$T = 150$ (2) K
Block, yellow
0.10 × 0.09 × 0.08 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)
$T_{min} = 0.238$, $T_{max} = 0.297$
7433 measured reflections
1054 independent reflections
962 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.9°$
$h = -12 \rightarrow 12$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.048$
$S = 1.10$
1054 reflections
41 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0285P)^2 + 1.1841P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.74$ e Å^{-3}
$\Delta\rho_{min} = -1.36$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0029 (3)

Table 1
Selected geometric parameters (Å, °).

W1—S2	2.1856 (11)	W1—S1	2.2090 (10)
W1—S3	2.1870 (7)		
S2—W1—S3	109.25 (3)	S2—W1—S1	110.33 (4)
S3^{i}—W1—S3	108.23 (4)	S3—W1—S1	109.87 (2)

Symmetry code: (i) $x, \frac{3}{2} - y, z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···S2^{ii}	0.86	2.78	3.278 (3)	118
N1—H1N1···S3^{iii}	0.86	2.83	3.489 (3)	135
N1—H1N1···S3^{iv}	0.86	2.83	3.489 (3)	135
N1—H2N1···S2	0.86	2.57	3.242 (4)	136
N1—H2N1···S1	0.86	2.75	3.439 (3)	139
N1—H3N1···S3^{v}	0.86	2.65	3.414 (3)	149
N1—H3N1···S1^{v}	0.86	2.93	3.5552 (7)	131
N2—H1N2···S1	0.86	2.89	3.483 (4)	128
N2—H2N2···S3^{vi}	0.86	2.87	3.513 (3)	133
N2—H2N2···S3^{vii}	0.86	2.87	3.513 (3)	133
N2—H2N2···S1^{viii}	0.86	3.03	3.633 (4)	129
N2—H3N2···S3^{v}	0.86	2.82	3.563 (3)	146
N2—H3N2···S2^{v}	0.86	2.86	3.5289 (6)	136

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

The H atoms were located in a difference map and were refined with fixed bond lengths (N—H = 0.86 Å) and fixed isotropic displacement parameters [$U_{iso}(H) = 1.5U_{eq}(N)$] using a riding model. The maximum electron-density peak is located 0.98 Å from atom W1.

Data collection: *IPDS* (Stoe & Cie, 1998); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL*

(Bruker, 1998); software used to prepare material for publication: *XCIF* in *SHELXTL*.

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