

***trans*-Cyclohexane-1,4-diammonium
tetrathiotungstate(VI)****Bikshandarkoil R. Srinivasan,^{a*}
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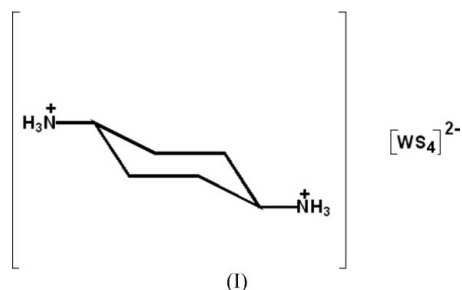
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Key indicatorsSingle-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$
 R factor = 0.023
 wR factor = 0.052
Data-to-parameter ratio = 32.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The structure of the title complex, $(\text{C}_6\text{H}_{16}\text{N}_2)[\text{WS}_4]$, consists of a tetrahedral $[\text{WS}_4]^{2-}$ dianion situated in a general position and two crystallographically independent *trans*-cyclohexane-1,4-diammonium cations located on centres of inversion. The anions are linked to the organic ammonium cations *via* $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds, resulting in the formation of alternating layers of cations and anions.

Comment

As part of an ongoing research programme, we are investigating the synthesis and structural characterization of organic ammonium tetrathiotungstates (Srinivasan *et al.*, 2005; Srinivasan, Näther *et al.*, 2006*a,b*). In the present report, we describe the structure of the title compound, (I), which is isostructural with the corresponding Mo compound, $(\text{C}_6\text{H}_{16}\text{N}_2)[\text{MoS}_4]$ (Srinivasan *et al.*, 2006).



The structure of (I) consists of a tetrahedral $[\text{WS}_4]^{2-}$ dianion situated in a general position and two crystallographically independent *trans*-cyclohexane-1,4-diammonium cations located on centres of inversion (Fig. 1). The cations adopt a chair conformation and their geometric parameters are in agreement with those in $(\text{C}_6\text{H}_{16}\text{N}_2)[\text{MoS}_4]$ (Srinivasan, Näther & Bensch, 2006). The WS_4 tetrahedron is slightly distorted, with $\text{S}-\text{W}-\text{S}$ angles between 107.06 (4) and 110.84 (5) $^\circ$ and $\text{W}-\text{S}$ bond lengths ranging from 2.1834 (12) to 2.2001 (11) \AA . These values are in good agreement with literature data (Srinivasan, Näther *et al.*, 2006*a*).

A total of ten short intermolecular $\text{S}\cdots\text{H}$ contacts ranging from 2.47 to 2.95 \AA are observed, all of which are less than the sum of their van der Waals radii (Bondi, 1964); the separation of 2.95 \AA is indicative of a weak hydrogen bond (Table 2). Each $[\text{WS}_4]^{2-}$ anion is linked to six different cations through nine $\text{N}-\text{H}\cdots\text{S}$ interactions (Fig. 2). All H atoms attached to the N atoms are involved in these hydrogen bonds, three of which are bifurcated. Each crystallographically independent cation is hydrogen-bonded to six different $[\text{WS}_4]^{2-}$ anions. The shortest $\text{W}-\text{S}$ distance is observed for S4, which is involved in

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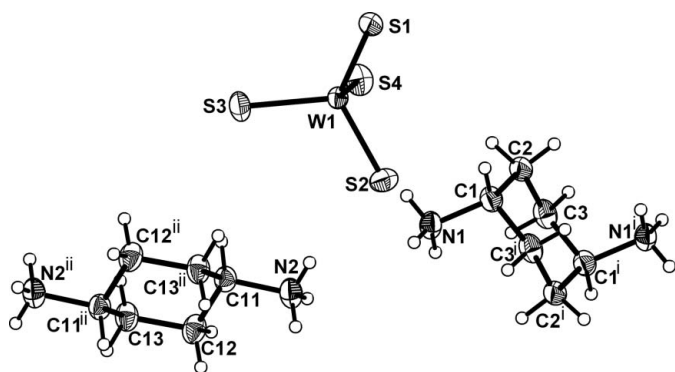


Figure 1
The structure of the constituent ions of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $2 - x, 3 - y, 2 - z$; (ii) $1 - x, 1 - y, 1 - z$.]

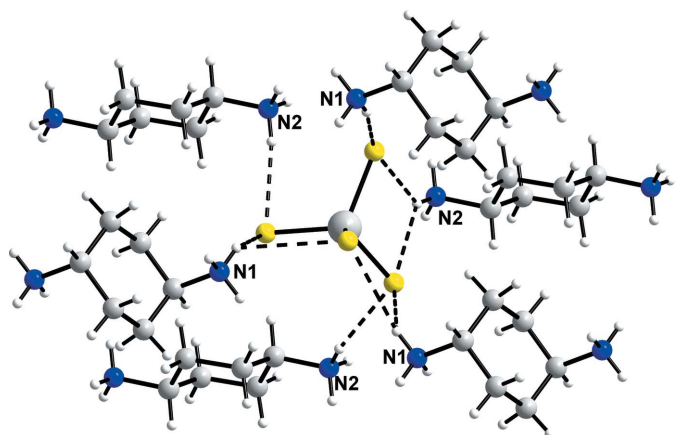


Figure 2
A view of the surroundings of the $[WS_4]^{2-}$ anion, showing the linking of each anion to six different cations *via* nine N—H...S hydrogen bonds (dashed lines).

two bifurcated hydrogen bonds, while all other S atoms make at least one singly shared hydrogen bond in addition to bifurcated hydrogen bonds. The observed W—S bond lengths can be attributed to the different numbers and strengths of hydrogen bonds between the H atoms of the cation and the S atoms. The W—S bond lengths tend to be longer when the S...H contacts are shorter and the N—H...S angles are more linear. As a result of the hydrogen-bonding interactions in (I), alternating layers of cations and anions are formed parallel to the (100) plane (Fig. 3).

Experimental

To ammonium tetrathiotungstate (348 mg, 1 mmol) in distilled water (15 ml), a few drops of aqueous ammonia were added and the solution was filtered. To the clear yellow filtrate *trans*-cyclohexane-1,4-amine (114 mg) was added and the reaction mixture was left aside for crystallization. After 1 d, yellow crystals of (I) separated slowly. The crystals were filtered off, washed with ice-cold water (2 ml) followed by propan-2-ol (10 ml) and diethyl ether (10 ml), and air-dried (yield 70%). The compound is air-stable and analyzed satisfactorily.

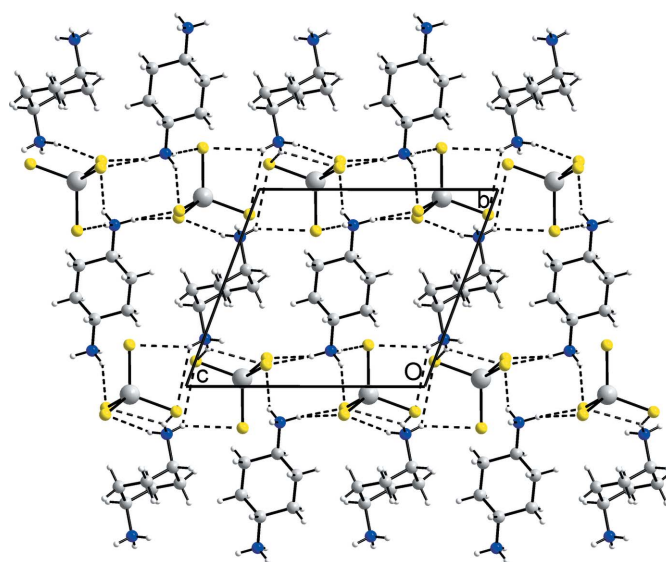


Figure 3
A packing diagram for (I), viewed along the a axis, showing the formation of alternating layers. N—H...S hydrogen bonds are shown as dashed lines.

Crystal data

$(C_6H_{16}N_2)[WS_4]$
 $M_r = 428.30$
Triclinic, $P\bar{1}$
 $a = 7.0354$ (9) Å
 $b = 9.6783$ (14) Å
 $c = 10.5523$ (19) Å
 $\alpha = 108.672$ (14)°
 $\beta = 92.673$ (14)°
 $\gamma = 106.228$ (12)°

$V = 646.22$ (17) Å³
 $Z = 2$
 $D_x = 2.201$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 9.55$ mm⁻¹
 $T = 293$ (2) K
Block, yellow
0.11 × 0.09 × 0.07 mm

Data collection

Stoe AED-II four-circle diffractometer
 ω/θ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)
 $T_{\min} = 0.365$, $T_{\max} = 0.502$
4059 measured reflections

3776 independent reflections
3105 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 30.0^\circ$
4 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.052$
 $S = 1.00$
3776 reflections
118 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.021P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.70$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.74$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

W1—S4	2.1834 (12)	W1—S3	2.2001 (11)
W1—S2	2.1913 (11)	N1—C1	1.514 (5)
W1—S1	2.1913 (10)	N2—C11	1.496 (5)
S4—W1—S2	109.45 (5)	S4—W1—S3	110.84 (5)
S4—W1—S1	110.01 (4)	S2—W1—S3	110.55 (5)
S2—W1—S1	107.06 (4)	S1—W1—S3	108.84 (4)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N1\cdots S3^i$	0.89	2.67	3.372 (4)	137
$N1-H1N1\cdots S4^i$	0.89	2.95	3.459 (3)	118
$N1-H2N1\cdots S1^{ii}$	0.89	2.53	3.399 (4)	167
$N1-H3N1\cdots S4$	0.89	2.78	3.600 (4)	155
$N1-H3N1\cdots S2$	0.89	2.81	3.357 (4)	121
$N2-H1N2\cdots S2^{iii}$	0.89	2.63	3.349 (4)	139
$N2-H1N2\cdots S1^{iii}$	0.89	2.72	3.424 (4)	137
$N2-H2N2\cdots S3^{ii}$	0.89	2.53	3.412 (4)	170
$N2-H3N2\cdots S2$	0.89	2.47	3.289 (4)	153
$C3-H3A\cdots S1^{ii}$	0.97	2.95	3.810 (4)	148

Symmetry codes: (i) $-x+1, -y+2, -z+2$; (ii) $x+1, y, z$; (iii) $-x+1, -y+2, -z+1$.

C- and N-bound H atoms were located in a difference map but they were placed in idealized positions, with C–H = 0.97 Å and N–H = 0.89 Å, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{N})$. There were practically no differences between the calculated positions and those found in a difference map.

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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References

- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
 Brandenburg, K. (1999). *DIAMOND*. Release 2.1c. Crystal Impact GbR, Bonn, Germany.
 Bruker (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Srinivasan, B. R., Dhuri, S. N., Poisot, M., Näther, C. & Bensch, W. (2005). *Z. Anorg. Allg. Chem.* **631**, 1087–1094.
 Srinivasan, B. R., Näther, C. & Bensch, W. (2006). *Acta Cryst.* **C62**, m98–m101.
 Srinivasan, B. R., Näther, C., Dhuri, S. N. & Bensch, W. (2006a). *Monatsh. Chem.* **137**, 397–411.
 Srinivasan, B. R., Näther, C., Dhuri, S. N. & Bensch, W. (2006b). *Polyhedron*, **25**, 3269–3277.
 Stoe & Cie (1998). *DIF4* (Version 7.09X/DOS), *REDU4* (Version 7.03) and *X-SHAPE* (Version 1.03). Stoe & Cie, Darmstadt, Germany.