

Synthesis and structural characterization of 1-methylpiperazinediium tetrasulfidotungstate monohydrate

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The reaction of $(\text{NH}_4)_2[\text{WS}_4]$ with 1-methylpiperazine results in the formation of 1-methylpiperazinediium tetrasulfidotungstate monohydrate, in good yield. $(\text{Me-pipH}_2)[\text{WS}_4]\cdot\text{H}_2\text{O}$ has been characterized by elemental analysis, IR, Raman and UV-vis spectra and its crystal structure. The title compound crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ and its structure consists of a discrete, slightly distorted tetrahedral tetrasulfidotungstate anion, 1-methylpiperazinediium cation and lattice water, which are linked by five varieties of H-bonding interactions namely $\text{N-H}\cdots\text{O}$, $\text{N-H}\cdots\text{S}$, $\text{O-H}\cdots\text{S}$, $\text{C-H}\cdots\text{O}$ and $\text{C-H}\cdots\text{S}$. The lattice water links pairs of organic cations with pairs of $[\text{WS}_4]^{2-}$ anions via $\text{N-H}\cdots\text{O}$, $\text{O-H}\cdots\text{S}$, and $\text{C-H}\cdots\text{O}$ bonds, while the cations and anions are linked via $\text{N-H}\cdots\text{S}$, and $\text{C-H}\cdots\text{S}$ bonds.

Keywords: Coordination chemistry, Crystal structure, H bonds, Tungsten, Tetrasulfidotungstates,

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The chemistry of group VI metal sulfides is a frontier area of research¹⁻⁶. As a part of an ongoing research program we are investigating the synthetic aspects, spectral characteristics, thermal properties and structural features of group VI tetrasulfidometalates, charge balanced by organic ammonium cations⁷⁻¹⁹. The relevance of organic tetrasulfidotungstates can be evidenced by their usefulness for the acquisition and analysis of natural abundance complex solid-state ³³S MAS NMR spectra⁶.

Organic tetrasulfidotungstates exhibit several weak H-bonding interactions between the $[\text{WS}_4]^{2-}$ anion and the organic cation in the form of several $\text{S}\cdots\text{H}$ distances, shorter than the sum of the van der Waals radii of S and H. These weak interactions can be varied by altering the steric bulk as well as the number of potential donor H atoms on the amine N atom of the organic cation. Based on this a rich

structural chemistry of tetrasulfidotungstates has been developed¹²⁻²³. Several $[\text{WS}_4]^{2-}$ compounds have been structurally characterized and the secondary interactions in these compounds have been reported. Most of these compounds crystallize in centrosymmetric space groups. It is interesting to note that all the reported $[\text{WS}_4]^{2-}$ compounds, excepting $(\text{C}_6\text{H}_{17}\text{N}_3)[\text{WS}_4]\cdot\frac{1}{2}\text{H}_2\text{O}$ ¹⁴ (trenH_2)[WS_4]. H_2O ¹⁶ and $[\text{Ce}(\text{DMF})_8]_2[\text{WS}_4]_3\cdot\text{H}_2\text{O}$ ²², are anhydrous, although most of the reported compounds are crystallized from aqueous medium. During the course of our investigations, we have observed that cations based on the cyclic diamine piperazine result in organic $[\text{WS}_4]^{2-}$ compounds with one very long W-S distance. Recently, we have synthesized a new organic tetrasulfidotungstate monohydrate, charge balanced by the 1-methylpiperazinediium cation, which exhibits five varieties of H-bond. The results of these studies are described herein.

Experimental

All the chemicals used in this study were of reagent grade and were used as received. Ammonium tetrasulfidotungstate was prepared by literature method²⁴. Far-IR spectra (80-500 cm^{-1}) were recorded using a Bruker IFS 66 infrared spectrometer in pressed polyethylene disks. Mid infrared spectra were collected in a KBr matrix using a Shimadzu (IR Prestige-21) FT-IR spectrometer and ATI Mattson Genesis infrared spectrometer in the range 4000-400 cm^{-1} . Raman spectra were recorded in the region 100-3500 cm^{-1} on a Bruker FRA 106 Fourier Transform Raman spectrometer. UV-visible spectra were obtained using a Shimadzu UV-2450 double beam spectrophotometer using matched quartz cells.

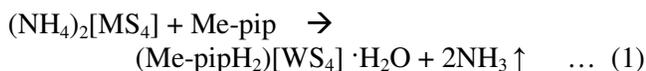
$(\text{Me-pipH}_2)[\text{WS}_4]\cdot\text{H}_2\text{O}$ (**1**) was prepared as follows: $(\text{NH}_4)_2[\text{WS}_4]$ (348 mg, 1 mmol) was dissolved in water (~15 mL) containing a few drops of ammonia and the solution was filtered. To the clear filtrate 1-methylpiperazine (0.7 mL) was added and the clear reaction mixture was left aside for crystallization resulting in the formation of yellow blocks of (**1**) in about two weeks. The crystalline product was filtered, washed with a little ice-cold water (2 mL) followed by 2-propanol (20 mL) and dried in air to obtain 200 mg of compound (**1**).

Anal.: Calc. for $(C_5H_{14}N_2)[WS_4] \cdot H_2O$ (**1**) MW 432.29; C 13.89; H, 3.73; N, 6.48; S, 29.67; Found: C, 13.80; H, 3.69; N, 6.40; S, 29.58 %. IR (cm^{-1}): 3316 (ν_{O-H}), 2987, 2910, 2804, 2652, 2557, 2421, 1630, 1564, 1447, 1390, 1364, 1303, 1245, 1172, 1106, 1000, 847, 696, 581, 465 (ν_3), 459, 448, 354., 187, 102. Raman (cm^{-1}): 3011, 2987, 2980, 2943, 2699, 1458, 1402, 1390, 1204, 1050, 1030, 1018, 776, 593, 480 (ν_1), 469 (ν_3), 444, 415, 176 (ν_2, ν_4), 128. UV-vis: (nm) (ϵ_{max} , $mol^{-1} L cm^{-1}$) 393 (17,000), 277 (25,400).

Intensity data for compound (**1**) were collected on an Image Plate Diffraction System (IPDS 1) from STOE using graphite-monochromated Mo- K_{α} radiation. A numerical absorption correction was performed and the structure was solved with direct methods using SHELXS-97²⁵ and refinement was done against F^2 using SHELXL-97²⁵. All non-hydrogen atoms were refined using anisotropic displacement parameters. The C-H hydrogen atoms were positioned with idealized geometry and were refined using a riding model. The N-H hydrogen atoms as well as the H atoms of the lattice water were located in difference map, their bond lengths were set to ideal values and afterwards they were refined using a riding model. Selected crystal refinement results for the title compound are summarized in Table 1.

Results and discussion

The synthetic methodology employed for the preparation of (**1**) is similar to the one reported for synthesis of several organic tetrasulfidometalates in our earlier work⁷⁻¹⁹. Thus, the reaction of an aqueous solution of $(NH_4)_2[WS_4]$ with 1-methylpiperazine followed by crystallization, resulted in base exchange, leading to the formation of the hydrated compound (**1**). In this base promoted cation exchange reaction, the stronger base, namely, 1-methylpiperazine, displaces the weaker ammonia resulting in the exchange of ammonium cations in $(NH_4)_2[WS_4]$ by the organic dication for charge balance Eq. (1).



Compound (**1**) which is crystallized from a strongly alkaline medium is not stable in acid and decomposes to insoluble metal sulfide product on acidification with dilute HCl. On reaction with an aqueous solution of $[Ni(en)_3]Cl_2$, compound (**1**) is converted quantitatively into the insoluble $[Ni(en)_3][WS_4]$ ¹⁴⁻¹⁶.

In addition, the title compound analyzed satisfactorily for the proposed formula.

The electronic spectrum of (**1**) exhibits characteristic signals which can be assigned for the transition of the $[WS_4]^{2-}$ chromophore^{14,15}. The IR spectrum of (**1**) exhibits several signals observed in the mid-infrared region above $500 cm^{-1}$ all of which can be attributed to the vibrations of the organic cation. The intense signal at around $3300 cm^{-1}$ in (**1**) may be assigned for ν_{O-H} . The low energy signals below $500 cm^{-1}$ are due to the vibrations of the $[WS_4]^{2-}$ moiety. For the free tetrahedral $[WS_4]^{2-}$ anion, four characteristic vibrations, $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$ and $\nu_4(F_2)$, are expected, all of which are Raman active while only ν_3 and ν_4 are IR active. The intense signal at $465 cm^{-1}$ in (**1**) is assigned to the triply degenerate $\nu_3(F_2)$ asymmetric stretching W-S vibration^{17,18}. The Raman spectrum of (**1**) exhibits an intense signal at $480 cm^{-1}$ which can be assigned for the symmetric stretching W-S vibration $\nu_1(A_1)$ while the intense signal at $181 cm^{-1}$ is assigned to the doubly degenerate $\nu_2(E)$ and $\nu_4(F_2)$ vibrations.

Table 1—Crystal data and structure refinement for $(Me-pipH_2)[WS_4] \cdot H_2O$ (**1**)

Empirical formula	$(C_5H_{14}N_2)[WS_4] \cdot H_2O$ (1)
Formula weight ($g mol^{-1}$)	432.29
Temperature (K)	170(2)
Wavelength (\AA)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (\AA)	8.1385(6)
b (\AA)	12.2345(8)
c (\AA)	12.8834(9)
β ($^\circ$)	98.206(9)
Volume (\AA^3)	1269.67(15)
Z	4
D_{calc} (mg/m^3)	2.261
Absorption coefficient (mm^{-1})	9.724
$F(000)$	824
Crystal size (mm^3)	$0.12 \times 0.1 \times 0.08$
Θ range for data collection ($^\circ$)	3.03 to 30.43
Index ranges	$-11 \leq h \leq 11, -17 \leq k \leq 17, -18 \leq l \leq 18$
Reflections collected	14782
Independent reflections (R_{int})	3820 (0.0319)
Completeness to theta	99.3 %
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	3820 / 0 / 119
Goodness-of-fit on F^2	1.081
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0309, wR2 = 0.0836$
R indices (all data)	$R1 = 0.0343, wR2 = 0.0855$
Extinction coefficient	0.0074(4)
Largest difference peak and hole ($e. \text{\AA}^{-3}$)	1.914 and -2.070

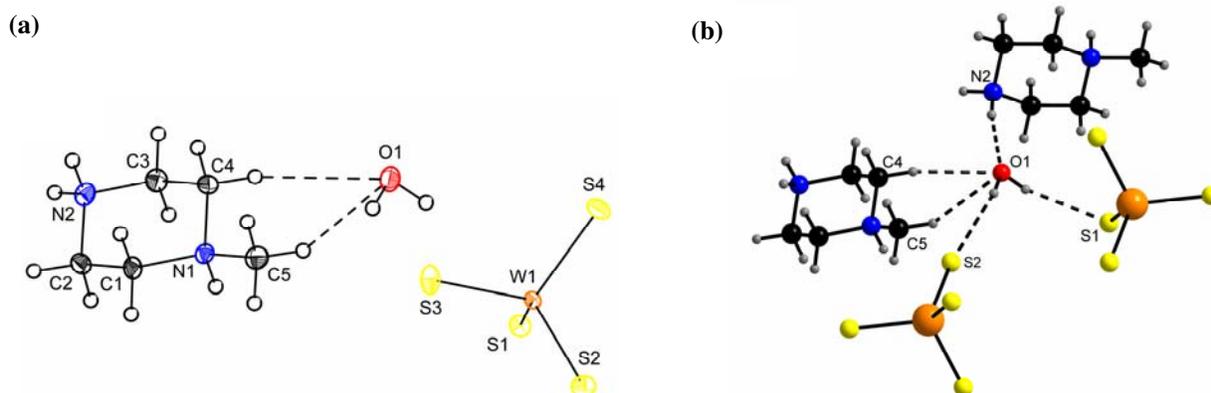


Fig. 1—(a) The crystal structure of (Me-pipH₂)[WS₄]·H₂O (**1**) showing the atom-labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown as broken lines. (b) The surroundings of the lattice water showing its linking to two different [WS₄]²⁻ anions and two organic cations via H-bonding shown in broken lines. [Colour code: C, black; N, blue; W, orange; S, yellow, O red].

The title compound crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with all atoms situated in general position. The crystal structure of (**1**) consists of a tetrahedral [WS₄]²⁻ dianion, a 1-methylpiperazinedium cation and lattice water (Fig. 1). The cyclic diamine adopts a chair confirmation with the methyl group occupying the equatorial position. Both the N atoms of 1-methylpiperazine are protonated as evidenced by the C-N bond distances which scatter in a narrow range between 1.492(5) and 1.507(5) Å (Table 2). The observed bond angles of the organic cation are in the normal range. The metric parameters of (**1**), indicate that the [WS₄]²⁻ tetrahedron is slightly distorted. The S-W-S bond angles range between 108.35(4) and 111.20(4)°. The W-S bond lengths vary from 2.1866(10) to 2.2026(11) Å with a mean value of 2.1953 Å. The difference between the longest and shortest W-S bond lengths is 0.0160 Å for compound (**1**) and this value is less than that observed in other tetrasulfidotungstates¹⁴⁻¹⁶ charge balanced by organic cations based on piperazine. In compound (**1**), two of the W-S bonds are longer than the average M-S bond length while the other two W-S bonds are shorter. Such a distribution of two long and two short M-S distances can be attributed to the weak secondary interactions between the organic cation and [WS₄]²⁻ anion, the details of which are described below.

An analysis of the structural features of several tetrasulfidotungstates reveals that organic [WS₄]²⁻ compounds exhibit a minimum of two varieties of H-bonds, viz., N-H...S and C-H...S^{14,19}. It is to be noted that compounds containing tetraalkylated N²⁰ or P²¹

Table 2—Selected bond lengths (Å) and angles (°) for (Me-pipH₂)[WS₄]·H₂O (**1**)

W(1)-S(4)	2.1866(10)	W(1)-S(3)	2.1986(10)
W(1)-S(2)	2.1935(10)	W(1)-S(1)	2.2026(11)
S(4)-W(1)-S(2)	109.07(4)	S(4)-W(1)-S(1)	108.90(4)
S(4)-W(1)-S(3)	110.55(4)	S(2)-W(1)-S(1)	108.35(4)
S(2)-W(1)-S(3)	111.20(4)	S(3)-W(1)-S(1)	108.71(4)
N(1)-C(5)	1.492(5)	C(5)-N(1)-C(1)	112.1(3)
N(1)-C(1)	1.500(5)	C(5)-N(1)-C(4)	110.4(3)
N(1)-C(4)	1.501(6)	C(1)-N(1)-C(4)	110.5(3)
C(1)-C(2)	1.516(6)	N(1)-C(1)-C(2)	110.9(3)
C(2)-N(2)	1.507(5)	N(2)-C(2)-C(1)	110.1(3)
N(2)-C(3)	1.492(5)	C(3)-N(2)-C(2)	111.0(3)
C(3)-C(4)	1.510(6)	N(2)-C(3)-C(4)	110.5(3)
		N(1)-C(4)-C(3)	110.9(3)

cations exhibit only C-H...S interaction, while some compounds like (pipH₂)[WS₄]¹⁵ exhibit N-H...N interaction in addition to N-H...S and C-H...S. We have earlier reported that substitution of one S atom in [WS₄]²⁻ by an O atom as in (enH₂)[WOS₃] can lead to more types of H-bonds²⁶. Alternatively, the presence of lattice water can also increase the varieties of H-bond as observed in the hydrated compounds (C₆H₁₇N₃)[WS₄]·½H₂O¹⁴ and (trenH₂)[WS₄]·H₂O¹⁶.

Compound (**1**) which is a monohydrate, contains eight hydrogen bond donors, namely, two ammonium groups, four methylene groups, a methyl group and a lattice water and two hydrogen acceptors, namely, tetrasulfidotungstate and crystal water. The [WS₄]²⁻ anion provides four acceptor sites and thus the entire molecular surface is decorated with hydrogen-bond donors and acceptors. An analysis of the crystal

Table 3—Hydrogen bonding geometry for (Me-pipH₂)[WS₄]²⁻·H₂O (**1**)

D-H...A	<i>d</i> (D-H) (Å)	<i>D</i> (H...A) (Å)	<i>D</i> (D...A) (Å)	<DHA (°)	Symmetry code
N1-H1...S2	0.930	2.456	3.230	140.75	-x+1, y-1/2, -z+1/2
N2-H2C...O1	0.920	1.902	2.792	162.27	-x, y-1/2, -z+1/2
N2-H2D...S1	0.920	2.749	3.373	125.99	x, -y+3/2, z+1/2
N2-H2D...S3	0.920	2.519	3.333	147.71	x, -y+3/2, z+1/2
O1-H101...S1	0.841	2.507	3.318	162.39	x, -y+5/2, z+1/2
O1-H201...S2	0.841	2.837	3.667	169.83	-x+1, y-1/2, -z+1/2
C1-H1A...S1	0.990	2.910	3.634	130.71	-x+1, -y+2, -z
C1-H1A...S2	0.990	2.890	3.684	137.85	-x+1, -y+2, -z
C1-H1B...S4	0.989	2.940	3.858	154.80	-x, -y+2, -z
C2-H2B...S2	0.990	2.759	3.599	142.99	x, y-1, z
C2-H2B...S3	0.990	2.886	3.870	173.05	-x+1, y-1/2, -z+1/2
C3-H3A...S2	0.990	2.999	3.678	126.74	-x+1, y-1/2, -z+1/2
C3-H3B...S3	0.990	2.958	3.910	161.49	-x, y-1/2, -z+1/2
C4-H4A...S1	0.990	2.786	3.673	149.44	-x, -y+2, -z
C4-H4B...S4	0.990	2.903	3.651	132.98	-x, y-1/2, -z+1/2
C4-H4B...O1	0.990	2.651	3.527	147.69	x, y, z
C5-H5A...S1	0.980	2.943	3.646	129.55	-x+1, -y+2, -z
C5-H5B...O1	0.980	2.535	3.426	151.08	x, y, z
C5-H5C...S4	0.979	2.986	3.875	151.58	-x+1, -y+2, -z

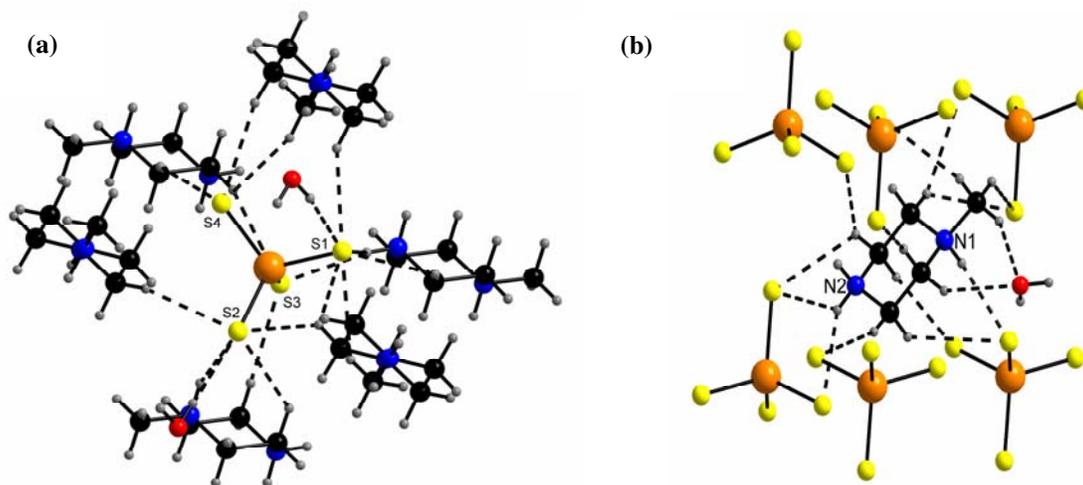


Fig. 2—(a) H-bonding situation around each [WS₄]²⁻ anion in (**1**) showing its linking to six different organic cations and two different lattice water via N-H...S, C-H...S, and O-H...S H-bonding. (b) H-bonding around the organic cation in (**1**) showing its linking to six different [WS₄]²⁻ anions and a lattice water with N-H...S, C-H...S, N-H...O and C-H...O interactions. [Colour code: C, black; H, medium grey; N, blue; W, orange; S, Yellow, O, red].

structure reveals that the organic cation, [WS₄]²⁻, and H₂O are linked with the aid of five varieties of H-bonding interactions consisting of three N-H...S, one N-H...O, two O-H...S, two C-H...O and eleven C-H...S bonds. The geometric parameters of these nineteen weak hydrogen bonding interactions are summarized in Table 3. The lattice water molecule is H-bonded to two different [WS₄]²⁻ anions via O-H...S

bonds while O1 atom of water functions as H-acceptor and is involved in H-bonding with two different organic cations via one N-H...O and two C-H...O bonds (Fig. 1). In (**1**), each [WS₄]²⁻ unit is hydrogen bonded to six different organic cations and two different H₂O molecules with the aid of three N-H...S, eleven C-H...S and two O-H...S interaction, while each 1-methylpiperazinium cation is hydrogen

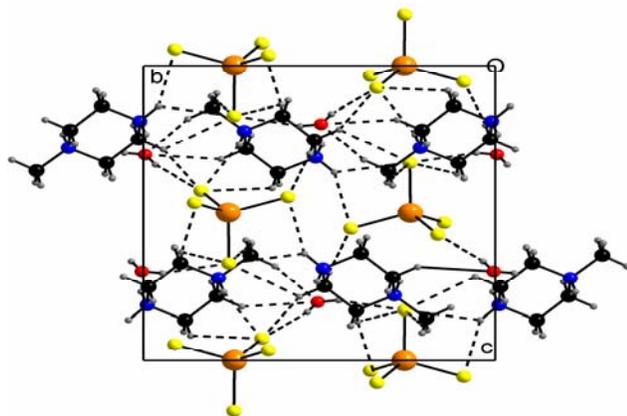


Fig. 3—Supramolecular structure of (1) depicting five varieties of H-bonding interactions (broken lines) in the crystallographic *bc* plane. [Colour code: C, black; H, medium grey; N, blue; W, orange; S, yellow; O, red].

bonded to six $[\text{WS}_4]^{2-}$ units and a lattice water via three N-H...S, eleven C-H...S, one N-H...O and two C-H...S interaction (Fig. 2). The S1 atom which makes the longest W-S bond is involved in one N-H...S and O-H...S bond at 2.749 and 2.507 Å respectively and three weak C-H...S bonds while the S4 atom with the shortest W-S bond at 2.1866(10) Å is involved only in three weak C-H...S interactions. As a result of the H-bonding interactions the organic cations and tetrasulfidotungstate anions are organized into alternating layers with the water molecules occupying the pores between the alternating layers (Fig. 3). The N-H...S and C-H...S interactions serve to link the layers of cations and anions.

The compound, 1-methylpiperazinedium tetrasulfidotungstate monohydrate described herein constitutes a new example of organic $[\text{WS}_4]^{2-}$ compound to the growing list of a series of structurally characterized tetrasulfidotungstates.

Supplementary material

Crystallographic data (excluding structure factors) for compound (1) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 745487. Copies of these data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

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