

Notes

Synthesis and characterization of a mixed cationic tetrasulfidotungstate monohydrate

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Synthesis and structural characterization of a mixed cationic tetrasulfidotungstate monohydrate (dabcoH)₃(NMe₄)[WS₄]₂·H₂O (dabco = 1,4-diazabicyclo[2.2.2]octane; NMe₄ = tetramethylammonium) is described. The compound crystallizes in the centrosymmetric monoclinic space group *P*2₁/*c* and its structure consists of three crystallographically independent monoprotonated (dabcoH)⁺ cations, a tetramethylammonium cation, two unique tetrasulfidotungstate anions, and a lattice water. The organic cations, [WS₄]²⁻ anion and lattice water are linked by several weak H-bonding interactions.

Keywords: Coordination chemistry; Crystal structure; Tetramethylammonium; Tetrasulfidotungstate

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As a part of an ongoing research program we are investigating the synthetic aspects, spectral characteristics, thermal properties and structural features of tetrasulfidotungstate, [WS₄]²⁻ charge balanced by organic ammonium cations¹⁻⁷. Organic [WS₄]²⁻ compounds are useful precursors for sulfide materials⁸ and have been investigated by solid state ³³S MAS NMR spectroscopy⁹. The reported synthesis and structural characterization of several [WS₄]²⁻ and corresponding isostructural Mo compounds charge balanced by a variety of organic ammonium ions demonstrates the flexibility of the tetrahedral [MS₄]²⁻ (M = Mo, W) unit to exist in a variety of structural environments^{1-7,10}. Organic tetrasulfidotungstates exhibit several weak H-bonding interactions between the [WS₄]²⁻ anion and the organic cation in the form of several short S···H distances. The observed distinct W-S bond distances attributed to the different secondary interactions around the S sites indicate the non-equivalence of the S atoms attached to W in the tetrahedral [WS₄]²⁻ compounds. Assignment of the solid state ³³S MAS NMR spectral resonances⁹ has confirmed the presence of the crystallographically reported non-equivalent S atoms in

bis(methylammonium) tetrasulfidotungstate¹¹. Presence of lattice water that can participate in H-bonding via O (as acceptor) and H (as donor) or two different cations can lead to additional or different secondary interactions in the form of short O···H (or S···H) contacts and thus can affect the environment around the S sites.

A majority of known organic tetrasulfidotungstates excepting (C₆H₁₇N₃)[WS₄].½H₂O (C₆H₁₇N₃ = 4-2(ammonioethyl) piperazin-1-ium)⁵ (Me-pipH₂)-[WS₄].H₂O (Me-pipH₂ = 1-methylpiperazinediium)⁷ and (trenH₂)[WS₄].H₂O (tren = tris(2-aminoethylamine))¹² crystallize as anhydrous compounds, although all compounds are synthesized by reaction of an aqueous solution of ammonium [WS₄]²⁻ with the corresponding amine. In addition, most of the reported organic tetrasulfidotungstate compounds contain either a single dication like 1-ethylpiperazinediium⁵ or a pair of monocations like *n*-propylammonium¹, dimethylammonium², ethylammonium³, ammonium¹³, etc. for charge balance. Examples of [WS₄]²⁻ containing two different cations are rare. In this note, we describe the synthesis and characterization of a new hydrated tetrasulfidotungstate charge balanced by two different cations, namely, (dabcoH)⁺ (dabco = 1,4-diazabicyclo[2.2.2]octane) and tetramethylammonium (NMe₄)⁺.

Experimental

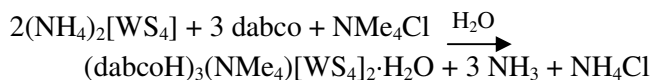
All the chemicals used in this study were of reagent grade and were used as received. (NH₄)₂[WS₄] was prepared by a literature procedure¹³. Intensity data for compound (1) were collected on an Image Plate Diffraction System (IPDS 1) from STOE using graphite-monochromated Mo-K_α radiation. A numerical absorption correction was performed. 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 and O-H hydrogen atoms were located in difference map, their bond lengths were set to ideal values and were refined using a riding model. The crystal investigated was slightly twinned and hence, a twin refinement was performed; BASF-parameter: 0.0284 (4). Crystal data of (1): C₂₂H₅₃N₇ONW₂S₈; *M* = 1055.89; monoclinic, space group: *P*2₁/*c*; *a* = 9.7188(6) Å; *b* = 26.5704(15) Å;

$c = 14.0382(8) \text{ \AA}$; $\alpha = \gamma = 90^\circ$; $\beta = 90.322(7)^\circ$; $V = 3625.1(4) \text{ \AA}^3$; $Z = 4$; $D_{\text{calc}} = 1.935 \text{ mg/m}^3$; $\mu = 6.832 \text{ mm}^{-1}$; $F(000) = 2072$; theta range for data collection ($^\circ$) = $2.23 - 28.11$; index range = $-12 \leq h \leq 12$, $-35 \leq k \leq 35$, $-18 \leq l \leq 18$; completeness to theta = 99.2 %; A total of 35515 reflections were collected of which 8775 were unique ($R_{\text{int}} = 0.0470$) and used for structure solution. Structure was solved using SHELXS-97¹⁴ and refinement was done against F^2 using SHELXL-97¹⁴ to $R1$ ($wR2$) = 0.0307 (0.0731) for 7463 reflections with $[I > 2\sigma(I)]$ using 363 parameters. R indices for all data $R1 = 0.0407$, $wR2 = 0.0773$; Goodness-of-fit on $F^2 = 1.025$; Maximum and minimum peaks were observed at 1.739 and $-1.824 \text{ e \AA}^{-3}$.

For the synthesis of $(\text{dabcoH})_3(\text{NMe}_4)[\text{WS}_4]_2 \cdot \text{H}_2\text{O}$ (**1**), $(\text{NH}_4)_2[\text{WS}_4]$ (348 mg, 1 mmol) was dissolved in water (~20 mL) containing a few drops of ammonia and the solution was filtered. To the clear filtrate, an aqueous solution (20 mL) containing dabco (0.168 g, 1.5 mmol) and NMe_4Cl (0.055 g, 0.5 mmol) was added and stirred well. The clear reaction mixture thus obtained was left undisturbed 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, followed by 2-propanol and dried in air to obtain compound (**1**) in ~15 % yield. Anal. Calc. for $\text{C}_{22}\text{H}_{53}\text{N}_7\text{OW}_2\text{S}_8$ (**1**) (MW 1055.89): C 25.02; H, 5.06; N, 9.29; S, 24.29; Found: C, 24.93; H, 5.11; N, 9.21; S, 24.58 %.

Results and discussion

The reaction of an aqueous solution of $(\text{NH}_4)_2[\text{WS}_4]$ with the cyclic amine dabco in the presence of NMe_4Cl resulted in the formation of a mixed cationic tetrasulfidotungstate (**1**) as shown below.



The analytical data of the product is indicative of the formation of an organic $[\text{WS}_4]^{2-}$ compound containing two different cations in a 3:1 ratio. The electronic spectrum exhibits signals, characteristic of the $[\text{WS}_4]^{2-}$ chromophore. The signals above 500 cm^{-1} in the IR spectrum can be attributed to the vibrations of the organic cations. The intense signal around 3500 cm^{-1} can be assigned for $\nu_{\text{O-H}}$, while the band at around 462 cm^{-1} can be assigned for the triply degenerate asymmetric stretching W-S vibration.

Compound (**1**) crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ and its structure consists of three crystallographically independent monoprotonated dabco cations, a tetramethylammonium cation, two unique tetrasulfidotungstate anions, and a lattice water with all atoms situated in general positions (Fig. 1). In each of the three cyclic cations only one of the two N atoms of dabco is protonated. This can also be evidenced from the C-N bond distances which range between 1.470(6)

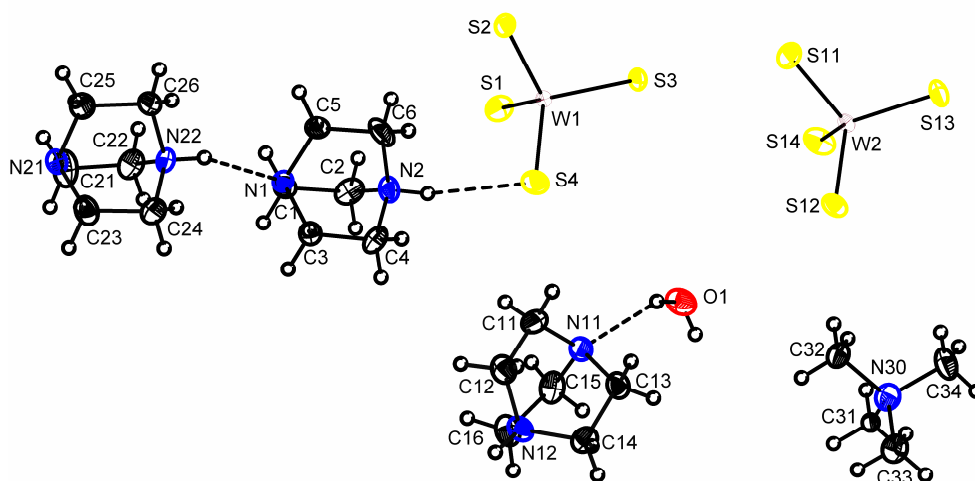


Fig. 1 — The crystal structure of $(\text{dabcoH})_3(\text{NMe}_4)[\text{WS}_4]_2 \cdot \text{H}_2\text{O}$ (**1**) showing the atom-labeling scheme. [Displacement ellipsoids are drawn at the 50 % probability level. H atoms are shown as circles of arbitrary radii. Intramolecular H-bonding is shown as dashed lines].

and 1.507(7) Å (Table 1). The observed bond angles of the organic cations are in the normal range. The S–W–S bond angles ranging from 107.38(5) to 111.12(6)° in the first anion and the S–W–S angles between 107.91(5) and 111.44(5) indicate a slight distortion of the (WS₄) tetrahedron. In the first anion, the W–S bond lengths vary from 2.1835(12) to 2.2107(13) Å with a mean value of

2.1912 Å while in the second crystallographically unique [WS₄]²⁻ anion the W–S bond distances range between 2.1699(13) and 2.2091(12) Å with an average W–S bond length of 2.1874 Å. It is interesting to note that all the known hydrated tetrasulfidotungstates crystallize in centrosymmetric space groups (Table 2). The observed difference (Δ) between the longest and shortest W–S bond lengths of 0.0392 Å for one of the independent anions in (**1**) is the maximum as compared with the Δ values for other hydrated tetrasulfidotungstates. The observed distinct W–S bond distances in (**1**), can be attributed to the several weak secondary interactions between the organic cations and [WS₄]²⁻ anions, the details of which are described below.

Based on an analysis of the structural features of several tetrasulfidotungstates we have shown that several organic [WS₄]²⁻ compounds exhibit a minimum of two varieties of H-bonds namely N–H...S and C–H...S. The presence of lattice water can increase the varieties of H-bond as observed in the earlier reported hydrated compounds (C₆H₁₇N₃)[WS₄]²⁻·½H₂O⁵, (Me-pipH₂)[WS₄]²⁻·H₂O⁷, (trenH₂)[WS₄]²⁻·H₂O¹² and [Ce(DMF)₈]₂[WS₄]₃·H₂O¹⁵ (Table 2). Compound (**1**) which is a monohydrate, contains several hydrogen bond donors, namely, the H atoms attached to the C, N or O atoms of the cations or the lattice water and several hydrogen acceptors namely the S, O and N atoms of tetrasulfidotungstates, crystal water and the organic cations respectively. Thus the entire molecular surface is decorated with hydrogen-bond donors and acceptors. In the title compound the organic cations, [WS₄]²⁻ anions and the lattice H₂O are linked with the aid of six varieties of H-bonding interactions consisting of two N–H...S, one N–H...N, one O–H...N, one O–H...S, two C–H...O and seventeen C–H...S bonds.

Table 1—Selected bond lengths and angles for (dabcoH)₃(NMe₄)[WS₄]₂·H₂O (**1**)

Bond lengths (Å)			
W(1)–S(2)	2.1835(12)	W(2)–S(11)	2.1699(13)
W(1)–S(3)	2.1844(12)	W(2)–S(14)	2.1779(13)
W(1)–S(4)	2.1865(13)	W(2)–S(13)	2.1928(12)
W(1)–S(1)	2.2107(13)	W(2)–S(12)	2.2091(12)
N(1)–C(3)	1.470(6)	N(2)–C(4)	1.499(7)
N(1)–C(1)	1.472(6)	C(1)–C(2)	1.534(7)
N(1)–C(5)	1.485(6)	C(3)–C(4)	1.538(7)
N(2)–C(6)	1.476(7)	C(5)–C(6)	1.524(8)
N(2)–C(2)	1.491(7)		
N(11)–C(13)	1.455(7)	N(12)–C(12)	1.501(7)
N(11)–C(15)	1.479(8)	C(11)–C(12)	1.543(8)
N(11)–C(11)	1.480(7)	C(13)–C(14)	1.520(8)
N(12)–C(16)	1.490(7)	C(15)–C(16)	1.546(8)
N(12)–C(14)	1.491(7)		
N(21)–C(25)	1.446(7)	N(22)–C(26)	1.501(7)
N(21)–C(23)	1.455(7)	C(21)–C(22)	1.531(8)
N(21)–C(21)	1.468(7)	C(23)–C(24)	1.536(8)
N(22)–C(24)	1.492(7)	C(25)–C(26)	1.549(8)
N(22)–C(22)	1.497(7)		
N(30)–C(31)	1.507(7)	N(30)–C(34)	1.526(7)
N(30)–C(32)	1.518(7)	N(30)–C(33)	1.527(7)
Bond angles (°)			
S(2)–W(1)–S(3)	107.38(5)	S(11)–W(2)–S(14)	109.22(6)
S(2)–W(1)–S(4)	111.12(6)	S(11)–W(2)–S(13)	110.39(5)
S(3)–W(1)–S(4)	108.97(5)	S(14)–W(2)–S(13)	109.42(6)
S(2)–W(1)–S(1)	109.93(5)	S(11)–W(2)–S(12)	108.41(6)
S(3)–W(1)–S(1)	110.39(6)	S(14)–W(2)–S(12)	107.91(5)
S(4)–W(1)–S(1)	109.04(6)	S(13)–W(2)–S(12)	111.44(5)

Table 2—Structural features of hydrated tetrasulfidotungstates

Compound	Space group	W–S (long) (Å)	Diff., Δ (Å)	Sec. interaction	Ref.
(C ₆ H ₁₇ N ₃)[WS ₄] ²⁻ ·½H ₂ O	C2/c	2.2052	0.0304	N–H...S, C–H...S, N–H...O, O–H...S	5
(Me-pipH ₂)[WS ₄] ²⁻ ·H ₂ O	P2 ₁ /c	2.2026	0.0160	N–H...S, C–H...S, N–H...O, C–H...O, O–H...S	7
(trenH ₂)[WS ₄] ²⁻ ·H ₂ O	P2 ₁ /c	2.1997	0.0258	N–H...S, C–H...S, N–H...N, N–H...O, O–H...S	12
(dabcoH) ₃ (NMe ₄)[WS ₄] ₂ ·H ₂ O (1) ^a	P2 ₁ /c	2.2107 2.2091	0.0272 0.0392	N–H...S, N–H...N, O–H...N, O–H...S, C–H...S, C–H...O	This work
[Ce(DMF) ₈] ₂ [WS ₄] ₃ ·H ₂ O ^b	Pt	2.188 2.178 2.183	0.015 0.023 0.027	----	15

^aTwo crystallographically independent [WS₄]²⁻ ions.

^bThree unique [WS₄]²⁻ ions. The H atom coordinates are not reported.

Table 3—Hydrogen bonding geometry for (dabcoH)₃(NMe₄)[WS₄]₂·H₂O (I)

D-H...A (Å)	D(D-H) (Å)	D(H...A) (Å)	D(D...A) (Å)	<DHA (°)	Symmetry code
N2-H2N...S4	0.920	2.703	3.418	135	x, y, z
N12-H12N...S1	0.920	2.563	3.293	137	x+1, -y+0.5, z-0.5
N22-H22N...N1	0.920	1.961	2.846	161	x, y, z
O1-H101...N11	0.860	2.131	2.826	138	x, y, z
O1-H201...S12	0.860	2.531	3.381	170	-x+1, y+1, -z+1
C4-H4B...S2	0.979	2.890	3.616	132	x, 0.5-y, -0.5+z
C14-H14B...S2	0.980	2.812	3.704	152	1+x, 0.5-y, -0.5+z
C15-H15B...S2	0.980	2.905	3.871	169	x, 0.5-y, -0.5+z
C4-H4B...S3	0.979	2.987	3.762	137	x, 0.5-y, -0.5+z
C21-H21A...S3	0.980	2.796	3.706	155	-x, -0.5+y, 1.5-z
C31-H31A...S3	0.971	2.481	3.283	140	x, 0.5-y, -0.5+z
C22-H22A...S11	0.982	2.795	3.678	150	x, 0.5-y, -0.5+z
C24-H24B...S11	0.979	2.849	3.729	150	x, 0.5-y, -0.5+z
C5-H5A...S12	0.980	2.612	3.575	167	1-x, -0.5+y, 1.5-z
C31-H31C...S12	0.970	2.595	3.394	140	1-x, 1-y, 1-z
C4-H4A...S13	0.980	2.896	3.713	141	1-x, -0.5+y, 1.5-z
C14-H14A...S13	0.980	2.970	3.863	152	1-x, 1-y, 1-z
C1-H1A...S14	0.980	2.981	3.820	144	-x, 0.5+y, 1.5-z
C5-H5B...S14	0.980	2.621	3.556	160	-x, 0.5+y, 1.5-z
C13-H13B...S14	0.982	2.879	3.784	138	1-x, 1-y, 1-z
C32-H32A...S14	0.971	2.862	3.666	159	-1+x, y, z
C33-H33C...S14	0.970	2.808	3.740	161	1-x, 1-y, 1-z
C31-H31B...O1	0.969	1.818	2.770	166	1-x, 1-y, 1-z
C25-H25A...O1	0.980	2.691	3.305	121	1-x, -0.5+y, 1.5-z

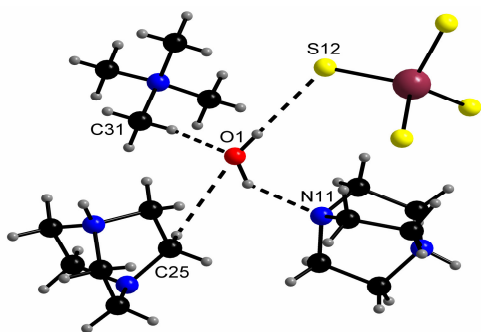


Fig. 2 — The surroundings of the lattice water showing its linking to a [WS₄]²⁻ anion, a (dabcoH)⁺ cation and two (NMe₄)⁺ cations via H-bonding (for details see Table 3) shown in broken lines.

Geometric parameters of these weak hydrogen bonding interactions are summarized in Table 3. The lattice water molecule is linked to a (NMe₄)⁺, two (dabcoH)⁺ cations and a [WS₄]²⁻ anion via two C-H...O, a O-H...N and a O-H...S interaction with O1 functioning as H-acceptor and the H of water functioning as donor (Fig. 2). In (I), the H-bonding situation around each of the independent [WS₄]²⁻ unit is different with one tetrasulfidotungstate (W1) linked to five (dabcoH)⁺ and one (NMe₄)⁺ with the aid of two N-H...S and six C-H...S interactions while the second unique anion (W2) is hydrogen bonded to four (dabcoH)⁺, two (NMe₄)⁺ and a water via one O-H...S and eleven C-H...S interactions (Fig. 3). The

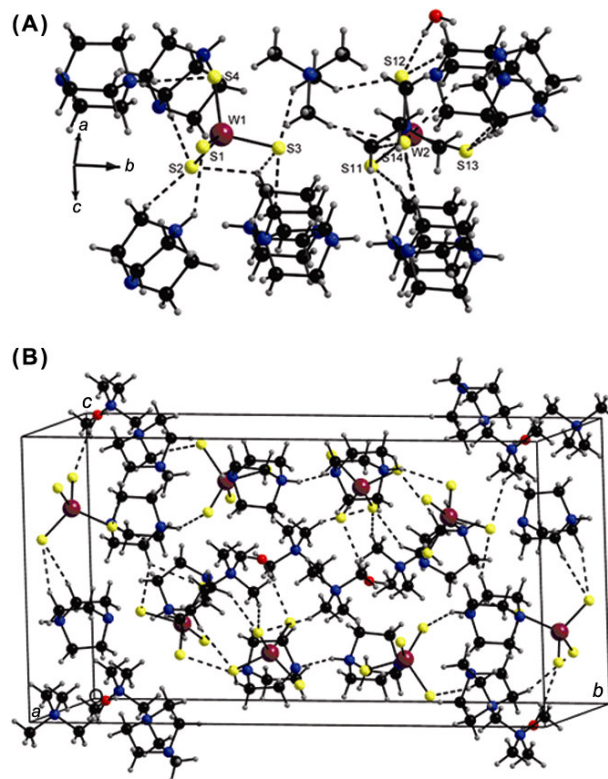


Fig. 3 — (A) H-bonding surroundings of the crystallographically independent [WS₄]²⁻ anions in (I). (B) A view of the crystallographic packing of (I) depicting the supramolecular structure.

single N-H...N interaction serves to link two adjacent (dabcoH)⁺ cations while the lone O-H...N interaction occurs between the lattice water and a (dabcoH)⁺ cation. As a result of the H-bonding interactions an intricate H-bonding network (Fig. 3) is observed. In summary, the mixed cationic tetrasulfidotungstate monohydrate (**1**) described herein constitutes a new example of [WS₄]²⁻ to the growing list of structurally characterized tetrasulfidotungstates.

Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre under CCDC 765454 (**1**). Copies of these data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: +44-(0)1223-336033; Email: deposit@ccdc.cam.ac.uk).

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