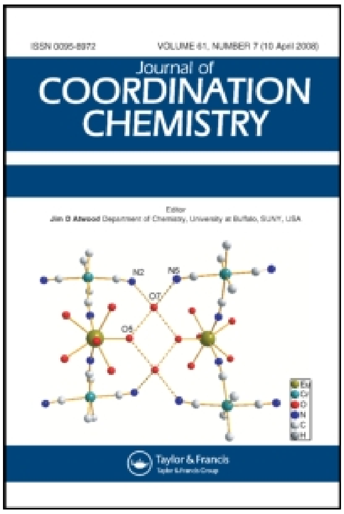

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Synthesis and characterization of bis(alkylammonium) tetrasulfidometalates

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The synthesis and characterization of the bis(alkylammonium) tetrasulfidometalates, $(EtNH_3)_2[MS_4]$ (M = W **1**, Mo **2**), $[BuNH_3]_2[MS_4]$ (M = W **3**; Mo **4**) and $(Et\text{-}enH_2)[WS_4]$ **1-en** (Et-en = N-ethylethane-1,2-diamine), are reported. Compound **1** crystallizes in the centrosymmetric orthorhombic space group *Pnma* and its structure consists of discrete slightly distorted tetrahedral $[WS_4]^{2-}$ of *m* symmetry, separated by two crystallographically independent $(EtNH_3)^+$ ions located on mirror planes. The carbons of one ethylammonium are disordered. Compound **1-en** crystallizes in the centrosymmetric orthorhombic space group *Pbca* with all atoms situated in general positions. Its structure consists of discrete $(Et\text{-}enH_2)^{2+}$ and a slightly distorted tetrahedral $[WS_4]^{2-}$ with the cations and anions linked by several weak hydrogen bonds.

Keywords: Crystal structure; Tetrasulfidotungstate; Hydrogen bonding interactions

1. Introduction

Sulfido compounds of Mo and W are a frontier area of research [1–5]. Recent work by the Jakobsen group on solid-state ^{33}S MAS NMR spectral characteristics of the tetrasulfidometalates of Mo and W [1, 2] has added a new dimension to the chemistry of these compounds. The importance of organic tetrasulfidometalates can be evidenced by the usefulness of bis(methylammonium) tetrasulfidotungstate for the acquisition and analysis of natural abundance solid-state ^{33}S MAS NMR spectra [2]. As part of our research in this area, we are investigating the synthesis, spectral characteristics, thermal properties, and structural aspects of tetrasulfido compounds of Mo and W [6–10]. The research has resulted in a rich structural chemistry of the tetrahedral $[MS_4]^{2-}$ (M = Mo, W) compounds charge balanced by organic ammonium cations [10–28].

In an earlier paper, we reported on synthesis and structural aspects of $(PrNH_3)_2[MS_4]$ ($PrNH_3$ = *n*-propylammonium; M = W or Mo) [27]. The isostructural bis(*n*-propylammonium) tetrasulfidometalates crystallize in the centrosymmetric orthorhombic space

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group *Pnma* and the structure consists of two crystallographically independent organic cations and a $[MS_4]^{2-}$ with the cations and anions located on mirror planes, resulting in two identical M–S distances in these compounds. This same structural feature of anion and cations lying on mirror planes is observed in K^+, Rb^+, Cs^+, ammonium and methylammonium $[MS_4]^{2-}$ compounds [26, 27, 29–37], all of which crystallize in the orthorhombic space group *Pnma* and exhibit two identical M–S distances (table 1). In the bis(alkylammonium) tetrasulfidometalates, the structures of the bis(methylammonium) [29, 30] and bis(*n*-propylammonium) [27] compounds were reported by us. In continuation of this work, we wish to report on the synthesis and spectral characterization of the bis(ethylammonium) and bis(butylammonium) tetrasulfidometalates and crystal structures of two new tetrasulfidotungstates, $(EtNH_3)_2[WS_4]$ ($EtNH_3$ = ethylammonium) and $(Et\text{-}enH_2)[WS_4]$ ($Et\text{-}enH_2$ = N-ethylethane-1,2-diaminium), in this article.

2. Experimental

2.1. *Materials and methods*

All chemicals used in this study were of reagent grade and used as received. The ammonium salts of the group VI tetrasulfidometalates were prepared by a published procedure [38]. Mid-infrared spectra were recorded in a KBr matrix using a Shimadzu (IR Prestige-21) FT-IR spectrometer and an ATI Mattson Genesis infrared spectrometer from 4000 to 400 cm^{-1}. Far-IR spectra (range 80–500 cm^{-1}) were recorded using a Bruker IFS 66 infrared spectrometer in pressed polyethylene discs. Raman spectra were recorded in the region 100–3500 cm^{-1} on a Bruker FRA 106 Fourier Transform Raman spectrometer. UV-Vis spectra were acquired on a Shimadzu UV-2450 double beam spectrophotometer using matched quartz cells. NMR spectra in D_2O or DMSO-d_6 were collected with a Bruker 300 MHz FT-NMR instrument.

Table 1. Structural features of alkali metal, ammonium and bis(alkylammonium) tetrasulfidometalates crystallizing in the orthorhombic space group *Pnma*.

Compound	M–S (long) (Å)	M–S (short) (Å)	Difference Δ (Å)	Refs.
$K_2[MoS_4]$	2.2000	2.1757	0.0243	[34]
$K_2[WS_4]$	2.1901	2.1758	0.0143	[26]
$Rb_2[WS_4]$	2.2053	2.1710	0.0343	[35]
$Rb_2[MoS_4]$	2.1917	2.1782	0.0135	[36]
$Cs_2[WS_4]$	2.2079	2.1915	0.0164	[31]
$Cs_2[MoS_4]$	2.1935	2.1809	0.0126	[37]
$(NH_4)_2[WS_4]$	2.2090	2.1856	0.0234	[32]
$(NH_4)_2[MoS_4]$	2.186	2.171	0.015	[33]
$(CH_3NH_3)_2[WS_4]$	2.2010	2.1862	0.0148	[29]
$(CH_3NH_3)_2[MoS_4]$	2.1961	2.1762	0.0199	[30]
$(EtNH_3)_2[WS_4]$[a]	2.187	2.178	0.009	This work
$(PrNH_3)_2[WS_4]$[a]	2.195	2.1869	0.0081	[27]
$(PrNH_3)_2[MoS_4]$[a]	2.1876	2.1833	0.0043	[27]

[a] Cations are disordered.

The $[MS_4]^{2-}$ content of all the complexes was estimated as the insoluble $[Ni(en)_3][MS_4]$ as described earlier [13, 21].

2.2. *Preparation of organic tetrasulfidometalates 1–4 and 1-en*

$(NH_4)_2[WS_4]$ (0.348 g, 1 mmol) was dissolved in a mixture of 70% ethylamine (1 mL) and water (~15 mL). After filtration, the clear yellow filtrate was set aside in a refrigerator (~10°C) for crystallization. The crystals of **1** which separated after a few days were filtered, washed with a small amount of ice-cold water (1 mL), followed by isopropyl alcohol (5 mL), diethylether (10 mL) and dried in air. Yield: 65%. The use of *n*-butylamine or N-ethylethane-1,2-diamine (Et-en) in the above reaction resulted in the formation of **3** and **1-en**, respectively. The Mo compounds **2** and **4** were prepared similarly by employing $(NH_4)_2[MoS_4]$ (0.260 g, 1 mmol) in place of $(NH_4)_2[WS_4]$. Compounds **2** and **4** were also prepared by passing H_2S gas for 30–40 min into an aqueous solution of ammonium heptamolybdate (1 g in 10 mL water) containing 70% ethylamine (4 mL) or *n*-butylamine (3 mL) maintained at 60°C. The reaction mixture was cooled, filtered, washed with ice-cold water, followed by isopropanol and ether, and dried as before.

Anal. Calcd for $C_4H_{16}N_2WS_4$ **1**: C, 11.88; H, 3.99; N, 6.93; WS_4, 77.20. Found: C, 11.353; H, 3.624; N, 6.278; WS_4, 76.9%. IR data (cm^{-1}): 3068 ($\upsilon_{(-NH3)}+$) 2803, 2843, 2769, 2738, 2669, 2642, 2519, 2422, 2360, 2337, 1797, 1556, 1462, 1392, 1178, 1043, 948, 866, 829, 785, 684, 460 (υ_3), 202, 101. Raman data (cm^{-1}): 2980, 2967, 2934, 2874, 1451, 870, 479 (υ_1), 181 (υ_2, υ_4). UV-Vis data (water) in nm ($mol^{-1}\,L\,cm^{-1}$): 393 (14,134), 278 (20,745), 216 (25,170).

Anal. Calcd for $C_4H_{14}N_2WS_4$ **1-en**: C, 11.94; H, 3.51; N, 6.96; WS_4, 77.58. Found: C, 12.001; H, 3.449; N, 6.727; WS_4, 76.79%. IR data (cm^{-1}): 3288 ($\upsilon_{(>NH2)}+$), 3232, 3010 ($\upsilon_{(-NH3)}+$), 2978, 2951, 2891, 2833, 2791, 2715, 2679, 2563, 2432, 2409, 2357, 2331, 1583, 1462, 1448, 1400, 1047, 982, 920, 895, 814, 451 (υ_3), 209, 152. Raman data (cm^{-1}): 2984, 2947, 2934, 2902, 2874, 2843, 1440, 1311, 1053, 897, 876, 479 (υ_1), 467, 453 (υ_3), 320, 212, 194, 184 (υ_2, υ_4), 170, 117. UV-Vis data (aq. NH_3) in nm ($mol^{-1}\,L\,cm^{-1}$): 393 (13,242), 278 (19,444), 216 (23,942).

Anal. Calcd for $C_4H_{16}N_2MoS_4$ **2**: C, 15.18; H, 5.10; N, 8.85; MoS_4, 70.86. Found: C, 15.73; H, 5.36; N, 9.26; MoS_4, 70.14%. IR data (cm^{-1}): 3061 ($\upsilon_{(-NH3)}+$), 2995, 2891, 2839, 2767, 2736, 2665, 2640, 2517, 2424, 2360, 1803, 1554, 1460, 1392, 1178, 1043, 966, 948, 864, 785, 478 (υ_3), 394, 138. Raman data (cm^{-1}): 2979, 2965, 2933, 2874, 1556, 1449, 1390, 1045, 951, 870, 789, 487 (υ_3), 467, 452 (υ_1), 184 (υ_2, υ_4). UV-Vis data (water) in nm ($mol^{-1}\,L\,cm^{-1}$): 469 (12,323), 318 (16,705), 242 (24,110).

Anal. Calcd for $C_8H_{24}N_2WS_4$ **3**: C, 20.87; H, 5.25; N, 6.08; WS_4, 67.79. Found: C, 20.984; H, 5.251; N, 5.783; WS_4, 67.07%. IR data (cm^{-1}): 3076 ($\upsilon_{(-NH3)}+$), 2962, 2931, 2870, 2727, 2361, 1815, 1558, 1463, 1390, 1157, 1072, 1041, 1002, 925, 898, 785, 749, 459 (υ_3), 207, 120. Raman data (cm^{-1}): 2961, 2931, 2903, 2873, 2862, 2772, 1565, 1449, 1305, 1162, 1073, 1039, 885, 866, 787, 477 (υ_1), 452 (υ_3), 180 (υ_2, υ_4). UV-Vis data (water) in nm ($mol^{-1}\,L\,cm^{-1}$): 393 (15,099), 278 (20,525), 216 (23,144).

Anal. Calcd for $C_8H_{24}N_2MoS_4$ **4**: C, 25.80; H, 6.49; N, 7.52; MoS_4, 60.19. Found: C, 26.256; H, 6.586; N, 7.298; MoS_4, 59.37%. IR data (cm^{-1}): 3068 ($\upsilon_{(-NH3)}+$), 2960, 2931, 2872, 2731, 2358, 1554, 1535, 1462, 1392, 1377, 1161, 1072, 925, 900, 482 (υ_3), 466, 345. Raman data (cm^{-1}): 2960, 2931, 2902, 2873, 1451, 1073, 866, 489 (υ_3), 466, 451

(υ_1), 183 (υ_2, υ_4). UV-Vis data (water) in nm ($\text{mol}^{-1}\,\text{L}\,\text{cm}^{-1}$): 469 (5370), 318 (7269), 242 (10,493).

2.3. *X-ray crystallography*

Intensity data for **1** and **1-en** were collected on an Imaging Plate Diffraction System from STOE using graphite-monochromated Mo-Kα radiation. The structures were solved with direct methods using SHELXS-97 [39] and refinement was done against F^2 using SHELXL-97 [39]. In **1** both carbons of one ethylammonium are disordered over two positions and refined using a split model. All non-hydrogen atoms were refined anisotropically. The hydrogens attached to N in **1** and **1-en** were located in the difference maps and refined isotropically using a riding model. The technical details of data acquisition and some selected crystal refinement results for **1** and **1-en** are summarized in table 2.

3. Results and discussion

3.1. *Description of crystal structures of 1 and 1-en*

Bis(ethylammonium) tetrasulfidotungstate crystallizes in the centrosymmetric orthorhombic space group *Pnma* and is isostructural with the corresponding

Table 2. Crystallographic data and structure refinement for **1** and **1-en**.

Compound	$(\text{EtNH}_3)_2[\text{WS}_4]$ (**1**)	$(\text{Et-enH}_2)[\text{WS}_4]$ (**1-en**)
Formula weight ($\text{g}\,\text{mol}^{-1}$)	404.28	402.26
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pbca*
Unit cell dimensions (Å)		
a	10.055(2)	9.5103(3)
b	7.1179(14)	10.0018(3)
c	17.870(4)	24.9292(7)
Volume (Å^3), Z	1279.0(5), 4	2371.28(12), 8
Calculated density ($\text{g}\,\text{cm}^{-3}$)	2.100	2.254
Absorption coefficient (mm^{-1})	9.640	10.398
$F(000)$	768	150
θ range for data collection (°)	2.32 to 29.26	1.63 to 29.18
Index ranges	$-13 \le h \le 13$, $-9 \le k \le 9$, $-24 \le l \le 24$	$-13 \le h \le 13$, $-13 \le k \le 12$, $-34 \le l \le 32$
Reflections collected	23,016	20,260
Independent reflections (R_{int})	1851 (0.0404)	3188 (0.0403)
Completeness to $\theta = 25.02$ (%)	98.9	99.7
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1851/0/70	3188/0/101
Goodness-of-fit on F^2	1.351	1.221
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0397$, $wR_2 = 0.0694$	$R_1 = 0.0317$, $wR_2 = 0.0572$
R indices (all data)	$R_1 = 0.0441$, $wR_2 = 0.0705$	$R_1 = 0.0384$, $wR_2 = 0.0590$
Largest difference peak and hole (e Å^{-3})	0.803 and −1.311	0.714 and −0.908

bis(methylammonium), bis(n-propylammonium) and alkali metal tetrasulfidotungstates (table 1). The structure of **1** consists of discrete slightly distorted tetrahedral $[WS_4]^{2-}$ of m symmetry, separated by two crystallographically independent ethylammonium cations situated on mirror planes (figure 1). In **1** the $[WS_4]^{2-}$ tetrahedron is slightly distorted and the S–W–S bond angles range between 108.36(9) and 110.29(6)°, while the W–S bonds vary from 2.178(2) to 2.187(2) Å with a mean W–S bond length of 2.1809 Å (table 3). The difference Δ between the longest and shortest W–S bond is 0.009 Å and is comparable with the Δ value of 0.0081 Å observed for the isostructural $(n\text{-prNH}_3)_2[WS_4]$. In view of the special position of the anion, two S atoms (S2) located on either side of the mirror plane are identical resulting is two equivalent W–S distances at 2.1793(16) Å, a structural feature observed in all the alkali metal, ammonium, and methylammonium $[MS_4]^{2-}$ compounds. In the series of isostructural bis(alkylammonium) tetrasulfidometalates, the ethylammonium and n-propylammonium cations are disordered. Analysis of the structure of **1** reveals short S···H distances. A detailed correlation of the effect of weak H-bonding interactions on the W–S distances in **1** is not described, in view of the observed disorder in the cation.

Compound **1-en** crystallizes in the centrosymmetric orthorhombic space group *Pbca* with all atoms situated in general positions. The closely related compounds $(\text{enH}_2)[WS_4]$ (enH_2 = ethylenediammonium) and $(\text{Me-enH}_2)[WS_4]$ (Me-enH_2 = N-methylethane-1,2-diaminium) containing cations based on en or substituted en crystallize in the non-centrosymmetric space group $P2_12_12_1$. The structure of **1-en** consists of a slightly distorted tetrahedral $[WS_4]^{2-}$ and a $(\text{Et-enH}_2)^{2+}$ (figure 2). The geometric parameters of the organic cation are in the normal range and both N atoms of Et-en are protonated resulting in a dication. The S–W–S angles range between 108.72(5) and 110.53(6)° (table 3), while the W–S distances scatter in a narrow range between 2.1734(12) and 2.1934(12) Å with a mean W–S bond length of 2.1857 Å. In **1-en**, two of the W–S bonds are shorter than the mean W–S distance of 2.1857 Å, while the other two sulfurs at longer distances indicate

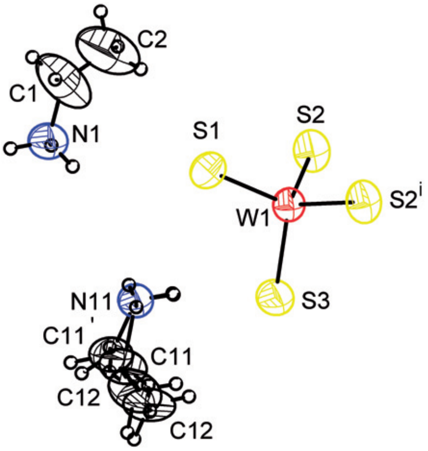


Figure 1. The crystal structure of $(EtNH_3)_2[WS_4]$ **1** showing the atom-labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. The C11 and C12 carbons of one of the cations are disordered. Color code: C, black; N, blue; W, red; S, yellow. Symmetry code: (i) x, $3/2 - y$, z.

a distorted WS_4 tetrahedron. The distribution of two short and two long W–S bonds in **1-en** can be attributed to the several weak hydrogen bonding interactions observed between the $[WS_4]^{2-}$ and $(Et\text{-}enH_2)^{2+}$. Scrutiny of the structure reveals a total of 14 weak S···H bonds comprising eight N–H···S and six C–H···S interactions, the

Table 3. Selected bond lengths and angles (Å, °).

$[(EtNH_3)]_2[WS_4]$ (**1**)			
W(1)–S(1)	2.178(2)	W(1)–S(2)	2.1793(16)
W(1)–S(3)	2.187(2)	W(1)–S(2)	2.1793(16)
S(1)–W(1)–S(2)^i	110.29(6)	S(2)^i–W(1)–S(2)	108.36(9)
S(1)–W(1)–S(2)	110.29(6)	S(2)–W(1)–S(3)	108.84(6)
S(1)–W(1)–S(3)	110.17(9)	S(2)^i–W(1)–S(3)	108.84(6)
$(Et\text{-}enH_2)[WS_4]$ (**1-en**)			
W(1)–S(1)	2.1734(12)	W(1)–S(2)	2.1917(12)
W(1)–S(3)	2.1844(12)	W(1)–S(4)	2.1934(12)
S(1)–W(1)–S(2)	108.72(5)	S(1)–W(1) –S(4)	110.53(6)
S(1)–W(1)–S(3)	109.27(5)	S(3)–W(1)–S(2)	110.00(5)
S(2)–W(1)–S(4)	108.74(5)	S(3)–W(1)–S(4)	109.58(5)

Symmetry transformations used to generate equivalent atoms: (i)x, $-y+3/2$, z.

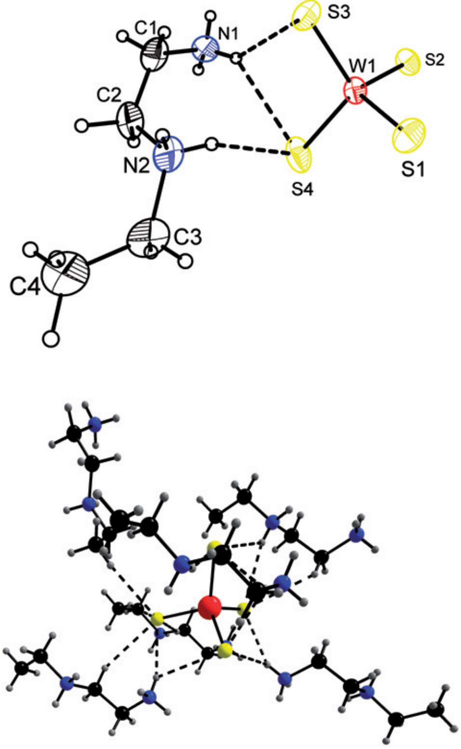


Figure 2. The crystal structure of $(Et\text{-}enH_2)[WS_4]$**1-en** showing the atom-labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown as broken lines (top). H-bonding situation around each $[WS_4]^{2-}$ anion in **1** showing its linking to six different organic cations *via* N–H···S, and C–H···S H-bonding (bottom). Color code: C, black; N, blue; W, red; S, yellow.

details of which are summarized in table 4. The S4, which makes the longest W–S distance of 2.1934 Å, is involved in three N–H···S interactions, while S3 and S2 have only two N–H···S bonds; S1 having the shortest bond to W shows only a single N–H···S interaction. Each $[WS_4]^{2-}$ is hydrogen bonded to six different $[\text{Et-enH}_2]^{2+}$ (figure 2), while each $(\text{Et-enH}_2)^{2+}$ cation displays H bonds to six different tetrasulfidotungstates *via* eight N–H···S and six C–H···S bonds resulting in an extended H-bonding network (figure 3).

3.2. *Synthesis and spectroscopy*

The reaction of $(NH_4)_2[MS_4]$ with aqueous RNH_2 (R = ethyl or *n*-butyl) (equation 1) followed by crystallization resulted in formation of **1**–**4** charge balanced by two alkylammonium cations. This synthetic methodology is identical to the one employed for the synthesis of bis(methylammonium) and bis(*n*-propylammonium) tetrasulfidometalates [27, 29]. The use of the diamine N-ethylethane-1,2-diamine (Et-en) resulted in the formation of **1-en** containing a diprotonated cation. Compounds **2** and **4** can also be prepared by passing a rapid stream of H_2S gas into a hot aqueous solution of molybdic acid or heptamolybdate containing ethylamine or *n*-butylamine.

$$(NH_4)_2[MS_4] + 2RNH_2 \rightarrow (RNH_3)_2[MS_4] + 2NH_3 \ (M = Mo, W). \qquad (1)$$

The compounds are not stable in acids and decompose to insoluble metal sulfide products on acidification with dilute HCl. However, on reacting with an aqueous solution of $[Ni(en)_3]Cl_2$, all compounds are converted quantitatively into the insoluble $[Ni(en)_3][MS_4]$. All compounds are soluble in water, aqueous ammonia, DMF and DMSO, but are insoluble in organic solvents, such as CH_3CN or $CHCl_3$.

NMR spectral data in DMSO-d_6 and D_2O (table 5) confirm the presence of the organic cations as well as the purity of the substances. The ^{1}H-NMR chemical shifts of the compounds in both solvents are nearly identical. The broad signal observed for $-NH_3$ in DMSO-d_6 spectra disappear when the spectra are recorded in D_2O, thus enabling the assignment of the chemical shift of the protons attached to N. The measured ^{13}C resonances are in the expected range confirming the spectral purity.

Table 4. Hydrogen-bonding geometry (Å, °) for **1-en**.

D–H···A	*d*(H···A)	*D*(D···A)	∠DHA	Symmetry code
N1–H1N1···S3	2.648	3.340	135	x, y, z
N1–H1N1···S4	2.813	3.545	141	x, y, z
N1–H2N1···S2	2.482	3.275	149	$x+1/2, -y+3/2, -z$
N1–H2N1···S3	2.969	3.524	122	$x+1/2, -y+3/2, -z$
N1–H3N1···S1	2.448	3.305	162	$-x+1/2, y+1/2, z$
N2–H1N2···S2	2.559	3.343	146	$-x+1/2, y-1/2, z$
N2–H1N2···S4	2.832	3.485	131	$-x+1/2, y-1/2, z$
N2–H2N2···S4	2.417	3.265	157	x, y, z
C1–H1A···S2	2.915	3.648	133	$x+1, y, z$
C1–H1B···S2	2.947	3.606	126	$-x+1/2, y-1/2, z$
C2–H2A···S1	2.820	3.768	166	$x+1, y, z$
C2–H2B···S1	2.830	3.699	150	$-x+1/2, y+1/2, z$
C4–H4A···S1	2.921	3.691	138	$x+1/2, y, -z+1/2$
C2–H4B···S1	2.831	3.735	157	$x+1, y, z$

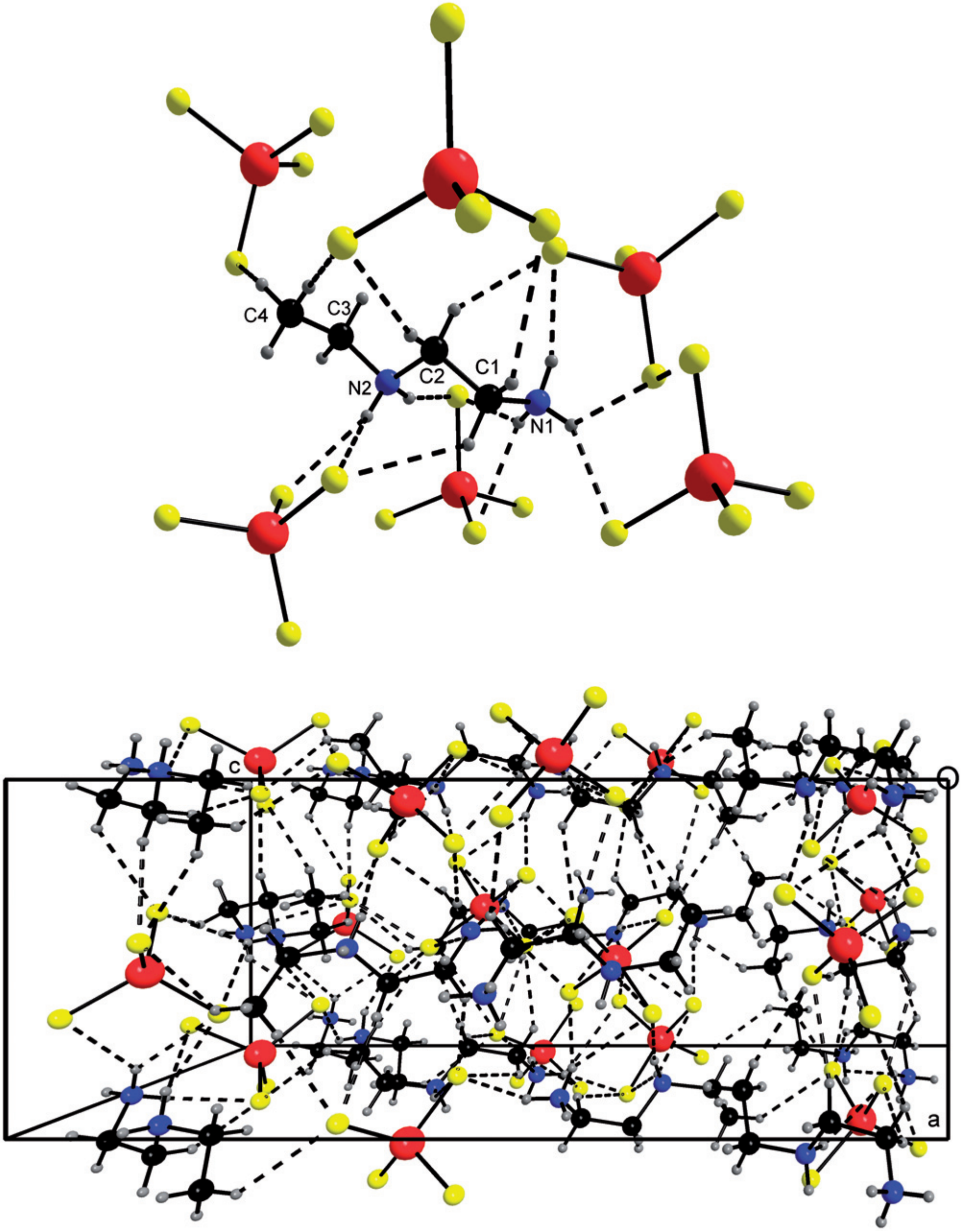


Figure 3. H-bonding situation around the organic cation in **1-en** showing its linking to six different $[WS_4]^{2-}$ anions *via* N–H $\cdots$ S and C–H $\cdots$ S H-bonding (top). A view along *b*-axis showing the crystallographic packing. H-bonding interactions are shown as broken lines (bottom). Color code: C, black; H, medium gray; N, blue; W, red; S, yellow.

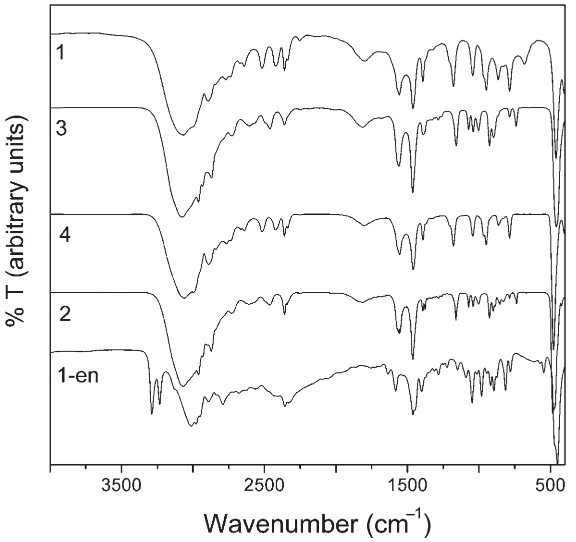
The electronic spectra of the W containing tetrasulfidometalates **1**, **3** and **1-en** exhibit signals at 393, 278 and 216 nm, assigned to intraligand charge transitions of $[WS_4]^{2-}$ [15–18, 38]. The UV-Vis spectra of **2** and **4** with signals at 469, 318, 242 nm are characteristic of the red $[MoS_4]^{2-}$ chromophore [12, 13, 38].

Table 5. Labeling scheme[a] and assignments of the ^{1}H-and ^{13}C-NMR spectral data.

	^{1}H-NMR data δ (ppm)		^{13}C-NMR data δ (ppm)
Compound	DMSO-d_6	D_2O	DMSO-d_6
$(EtN\backslash H_3)_2[WS_4]$	2.8 (H1, *q*, 7.2 Hz) 1.1 (H2, *t*, 7.2 Hz) 4.0 (–NH, br)	3.0 (H1, *q*, 7.2 Hz) 1.2 (H2, *t*, 7.2 Hz) –	35.2 (C1), 13.0 (C2)
$(EtNH_3)_2[MoS_4]$	2.8 (H1, *q*, 7.2 Hz) 1.1 (H2, *t*, 7.2 Hz) 3.5 (–NH, br)	2.9 (H1, *q*, 7.2 Hz) 1.1 (H2, *t*, 7.2 Hz) –	35.1 (C1), 13.5 (C2)
$(BuNH_3)_2[WS_4]$	2.8 (H1, *t*, 7.5 Hz) 1.5 (H2, *m*, 7.2 Hz) 1.3 (H3, *m*, 7.2 Hz) 0.8 (H4, *t*, 7.2 Hz) 3.5 (–NH, br)	2.9 (H1, *t*, 7.5 Hz), 1.5 (H2, *m*, 7.2 Hz), 1.3 (H3, *m*, 7.2 Hz), 0.8 (H4, *t*, 7.2 Hz), –	40.4 (C1), 29.6 (C2), 19.6 (C3), 13.9 (C4)
$(BuNH_3)_2[MoS_4]$	2.8 (H1, *t*, 7.5 Hz), 1.5 (H2, *m*, 7.8 Hz), 1.3 (H3, *m*, 7.2 Hz), 0.9 (H4, *t*, 7.5 Hz), 3.6 (–NH, br)	2.9 (H1, *t*, 7.2 Hz), 1.5 (H2, *m*, 7.8 Hz), 1.3 (H3, *m*, 7.2 Hz), 0.8 (H4, *t*, 7.5 Hz), –	41.6 (C1), 29.5 (C2), 19.5 (C3), 13.9 (C4)
$(Et\text{-}enH_2)[WS_4]$	2.8 (H1, *q*, 5.4 Hz) 2.79 (H2, *t*, 5.1 Hz) 2.7 (H3, *q*, 6.9 Hz) 1.1 (H4, *t*, 7.2 Hz) 4.2 (–NH, br)	2.9 (H1, *t*, 5.4 Hz) 2.89 (H2, *t*, 5.1 Hz) 2.7 (H3, *q*, 6.9 Hz) 1.1 (H4, *t*, 7.2 Hz) –	47.2 (C1), 43.3 (C2), 35.2 (C3), 14.1 (C4)
$H_3\overset{2}{C}-\overset{1}{C}H_2-\overset{+}{N}H_3$ **$(EtNH_3)^+$**	$H_3\overset{4}{C}-\overset{3}{C}H_2-\overset{+}{N}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2-\overset{+}{N}H_3$ **$(Et\text{-}enH_2)^{2+}$**		$H_3\overset{4}{C}-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2-\overset{+}{N}H_3$ **$(BuNH_3)^+$**

[a] Numerical label of H atom is same as that of the C atom to which it is attached.

IR spectra of the samples exhibit several signals in the mid-infrared region above 500 cm^{-1} (figure 4), all of which can be attributed to organic cations. IR spectra of **1**–**4** are nearly identical and exhibit a strong and broad signal centered around 3060 and 3010 cm^{-1} in **1-en** assignable for N–H stretching of the ammonium $(–NH_3)^+$ functionality. Compound **1-en** shows additional signals in the N–H region around 3288 and 3232 cm^{-1}, which can be attributed to the protonated secondary amine $(>NH_2)^+$. The low energy signals below 500 cm^{-1} are due to vibrations of the $[MS_4]^{2-}$. The intense signal due to W–S stretching vibration occurs at slightly lower energies (around 460 cm^{-1}) as compared to the corresponding Mo counterpart (around 480 cm^{-1}). For the free tetrahedral $[MS_4]^{2-}$ anion, four characteristic vibrations $\upsilon_1(A_1)$, $\upsilon_2(E)$, $\upsilon_3(F_2)$, and $\upsilon_4(F_2)$ are expected, all of which are Raman active, while only υ_3 and υ_4 are IR active. When the tetrahedron is distorted, the symmetry is slightly reduced, resulting in additional signals in the M–S region of the IR spectrum, including the appearance of the symmetric stretching M–S vibration $\upsilon_1(A_1)$ as a signal of weak to medium intensity. The triply degenerate $\upsilon_3(F_2)$ asymmetric stretching M–S vibration is readily observed in all compounds as an intense signal, while the symmetric stretching M–S vibration $\upsilon_1(A_1)$ occurs as an intense signal in the Raman spectra (figure 4). Thus, Raman spectral data in combination with the infrared data serve to assign the vibrations (see Section 2) of the $[MS_4]^{2-}$ moiety.



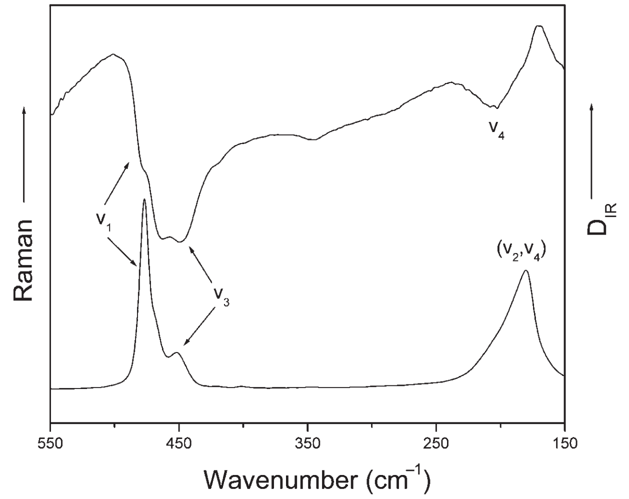


Figure 4. Comparative infrared spectra of $(EtNH_3)_2[WS_4]$ **1**, $(BuNH_3)_2[WS_4]$ **2**, $(EtNH_3)_2[MoS_4]$ **3**, $(BuNH_3)_2[MoS_4]$ **4**, and $(Et\text{-}enH_2)[WS_4]$ **1-en** (top). Infrared and Raman spectra of $(BuNH_3)_2[WS_4]$ **2** (bottom).

4. Conclusions

We have described the synthesis and spectral characteristics of $(RNH_3)_2[MS_4]$ (R = ethyl or *n*-butyl; M = Mo, W) and the single crystal structure of $(EtNH_3)_2[WS_4]$ and $(Et\text{-}enH_2)[WS_4]$ ($Et\text{-}enH_2$ = N-ethylethane-1,2-diaminium). The structurally characterized tetrasulfidotungstates described in this work constitute two new examples to the growing list of structurally characterized organic tetrasulfidotungstates.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos CCDC 748311 (**1-en**) and CCDC 748312 (**1**). Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK Fax: +44-1223-336033 or Email: deposit@ccdc.cam.ac.uk.

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