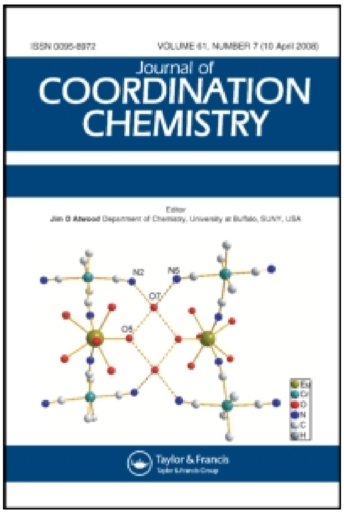

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Synthesis and structural characterization of bis(dimethylammonium) tetrasulfidometalates

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Reaction of $(NH_4)_2[MS_4]$ (M = Mo, W) with aqueous dimethylamine $(CH_3)_2NH$ or KOH results in the formation of bis(dimethylammonium) tetrasulfidometalates $[(CH_3)_2NH_2]_2[MS_4]$ (M = W **1**; Mo **2**) or dipotassium tetrasulfidotungstate $K_2[WS_4]$ (**3**). Compounds **1**–**3** were characterized by elemental analysis, IR and UV-Vis spectra and their crystal structures were determined. Compounds **1** and **2** are isostructural and crystallize in the centrosymmetric monoclinic space group *P2₁/n*. The structures consist of two crystallographically independent dimethylammonium cations and a slightly distorted tetrahedral $[MS_4]^{2-}$ anion with all atoms situated in general positions. The cations and anions are involved in several weak N–H ··· S and C–H ··· S interactions. Compound **3** crystallizes in the centrosymmetric orthorhombic space group *Pnma* and is isostructural with the previously reported $K_2[MoS_4]$. The structure of **3** consists of discrete slightly distorted tetrahedral $[WS_4]^{2-}$ anions of *m* symmetry, separated by two crystallographically independent K^+ cations located on mirror planes. A comparative description of the alkali metal, ammonium, methyl and dimethylammonium tetrasulfidometalates is presented.

Keywords: Dimethylamine; Crystal structure; Dipotassium tetrasulfidotungstate; Hydrogen bonding interactions

1. Introduction

Recent reports on the use of $(NH_4)_2[MS_4]$ (M = Mo, W) for advancements in natural abundance solid state ^{33}S MAS NMR spectroscopy [1, 2] have generated renewed interest in the chemistry of these familiar compounds, known since the nineteenth century [3, 4]. The tetrahedral $[MS_4]^{2-}$ dianions are well known for their use as starting materials for preparation of a variety of metal-sulfur compounds including catalytically important group VI metal sulfide materials [5–12]. Tetrasulfidometalates are used in therapy [13] and are employed as sulfur transfer reagents in organic synthesis [14]. As a part of our research in this area [15–18], we are investigating the synthesis, spectral characteristics, and thermal properties of group VI metal chalcogenides and have developed a convenient method for the facile synthesis of crystalline tetrahedral

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Table 1. Comparative structural parameters of alkali metal, ammonium, methylammonium, and dimethylammonium tetrasulfidotungstates.

Compound	Space group	M–S (long) (Å)	M–S (short) (Å)	Diff. Δ (Å)	Secondary interactions	Ref.
$(K)_2[MoS_4]$	*Pnma*	2.2000	2.1757	0.0243	K···S	[46]
$(K)_2[WS_4]$	*Pnma*	2.1901	2.1758	0.0143	K···S	This work
$Rb_2[WS_4]$	*Pnma*	2.2053	2.1710	0.0343	Rb···S	[47]
$Rb_2[MoS_4]$	*Pnma*	2.1917	2.1782	0.0135	Rb···S	[48]
$Cs_2[WS_4]$	*Pnma*	2.2079	2.1915	0.0164	Cs···S	[43]
$Cs_2[MoS_4]$	*Pnma*	2.1935	2.1809	0.0126	Cs···S	[49]
$(NH_4)_2[WS_4]$	*Pnma*	2.2090	2.1856	0.0234	N–H···S	[44]
$(NH_4)_2[MoS_4]$	*Pnma*	2.186	2.171	0.015	N–H···S	[45]
$(CH_3NH_3)_2[WS_4]$	*Pnma*	2.2010	2.1862	0.0148	N–H···S, C–H···S	[41]
$(CH_3NH_3)_2[MoS_4]$	*Pnma*	2.1961	2.1762	0.0199	N–H···S, C–H···S	[42]
$[(CH_3)_2NH_2]_2[WS_4]$	$P2_1/n$	2.2176	2.1822	0.0354	N–H···S, C–H···S	This work
$[(CH_3)_2NH_2]_2[MS_4]$	$P2_1/n$	2.2161	2.1776	0.0385	N–H···S, C–H···S	This work

$[MS_4]^{2-}$ compounds stabilized by organic ammonium cations [19–24]. Our method involves direct reaction of aqueous $(NH_4)_2[MS_4]$ with an organic amine and has resulted in the structural characterization of several new organic tetrasulfidometalates. Prior to our work, reactions of tetraalkylammonium hydroxide with $[MS_4]^{2-}$ or tetraalkylammonium halide with $[MS_4]^{2-}$ in aqueous or non-aqueous media were shown to result in the formation of organic soluble $[R_4N]_2[MS_4]$ (R = alkyl) compounds [25–27].

The organic $[MS_4]^{2-}$ compounds exhibit several weak H-bonding interactions between $[MS_4]^{2-}$ and the organic ammonium cation [19–24, 28–42]. These interactions (especially N–H···S) can be tuned by varying the steric bulk as well as the number of potential donor H atoms on the amine, with the organic cations functioning as handles to distort the $[MS_4]^{2-}$ tetrahedron, as evidenced by the observation of distinct W–S or Mo–S distances in several compounds. In earlier work, we have investigated the reactions of $(NH_4)_2[MS_4]$ with several acyclic and cyclic di-, tri-, and tetra-amines. However, only a few tetrasulfidometalates derived from monoamines like methylamine, isopropylamine, benzylmethylamine, etc. have been reported. A scrutiny of the structural features of $[MS_4]^{2-}$ compounds shows that $(NH_4)_2[MS_4]$ compounds are isostructural with the corresponding alkali metal tetrasulfidometalates $(M')_2[MS_4]$ (M′ = K, Rb or Cs) [43–49] and bis(methylammonium) tetrasulfidometalates $[(CH_3)NH_3]_2[MS_4]$ [41, 42] and crystallize in the centrosymmetric space group *Pnma* (table 1). In this series of compounds the structure of $K_2[WS_4]$ has not been reported. In all these isostructural compounds the cations and $[MS_4]^{2-}$ anions are situated on mirror planes. Recently, we reported on group VI tetrasulfidometalates stabilized by methylammonium cation, which exhibit several C–H···S interactions in addition to N–H···S bonds [41, 42]. In continuation of this work, we report the reactions of $(NH_4)_2[MS_4]$ with dimethylamine $(CH_3)_2NH$ 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 [25]. Infrared spectra were recorded in a KBr matrix using a Shimadzu (IR Prestige-21) Fourier Transform InfraRed (FT-IR) spectrometer. UV-Vis spectra were recorded on a Shimadzu UV-2450 double beam spectrophotometer using matched quartz cells.

2.2. *Preparation of bis(dimethylammonium) tetrasulfidotungstate (1)*

$(NH_4)_2[WS_4]$ (1 g, 2.87 mmol) was dissolved in a mixture of 40% dimethylamine (5 mL) and water (2 mL). After filtration, the clear yellow filtrate was left undisturbed in a refrigerator (~10°C) for crystallization. After a day, crystalline blocks of the title compound was separated out. The product was filtered, washed with ice-cold water (1 mL), followed by isopropyl alcohol (5 mL), diethyl ether (10 mL) and air-dried. Yield: 1.1 g (95%). Anal. Calcd for $[(CH_3)_2NH_2]_2[WS_4]$ (%): **1** : C 11.88; H, 3.99; N, 6.93; WS_4 77.20; Found: C, 11.85; H, 3.88; N, 6.77; WS_4, 77.06%. IR data (cm^{-1}): 3024 (ν_{N-H}), 2990, 2949, 2849, 2818, 2795, 2752, 2428, 2334, 1537, 1454, 1410, 1400, 1238, 1080, 1009, 880, 812, 478 (ν_1), 461 (ν_3), 448. UV-Vis data are given in nm ($mol^{-1}\,L\,cm^{-1}$): 394 (17,105), 279 (25,290), 217 (30,890).

2.3. *Preparation of bis(dimethylammonium) tetrasulfidomolybdate (2)*

The reaction of freshly prepared $(NH_4)_2[MoS_4]$ (1.04 g, 4 mmol) instead of $(NH_4)_2[WS_4]$ with 40% dimethylamine under identical conditions as above, followed by crystallization, resulted in the formation of compound **2** in 85% yield. Alternatively, **2** can also be prepared starting from MoO_3. Molybdic acid (3 g, 18.5 mmol) was dissolved in a mixture of water (5 mL) and 40% dimethylamine (10 mL) in a conical flask. Into this clear solution, a continuous and rapid stream of H_2S gas was passed for 40 min by maintaining the reaction mixture at ~60°C. When the red solid started appearing, the gas flow was stopped, the flask was stoppered, and the reaction mixture was allowed to cool in an ice-bath for ~30 min resulting in the separation of red polycrystalline **2**. The product was filtered, washed with isopropyl alcohol (10 mL), ether (10 mL), and dried under vacuum. The red filtrate was left in a refrigerator (~10°C) for further crystallization. After a day, deep red blocks of **2** suitable for single crystal X-ray study were obtained and isolated as before. Total yield ~5.7 g (97%). Anal. Calcd for $[(CH_3)_2NH_2]_2[MoS_4]$ (%): **2**: C, 15.18; H, 5.10; N, 8.85; S, 40.54; MoS_4, 70.86; Found: C, 15.10; H, 5.07; N, 8.17; MoS_4, 70.09%. IR data (cm^{-1}): 3021 (ν_{N-H}), 2984, 2949, 2843, 2816, 2793, 2749, 2428, 2330, 1537, 1450, 1420, 1398, 1236, 1080, 1009, 880, 851, 812, 480 (ν_3), 467 (ν_1), 447. UV-Vis data are given in nm ($mol^{-1}\,L\,cm^{-1}$): 469 (12,210), 317 (16,600), 242 (23,620).

2.4. *Preparation of dipotassium tetrasulfidotungstate (3)*

$(NH_4)_2[WS_4]$ (348 mg, 1 mmol) was dissolved in water (8 mL) containing KOH (112 mg, 2 mmol). The clear yellow solution thus obtained was warmed on a water bath at ~60°C for 15–20 min to expel ammonia gas. The warm reaction mixture was allowed to cool to room temperature and left undisturbed in a refrigerator. After a week, yellow crystalline blocks of **3** were isolated by using a similar procedure as for **1**. Anal. Calcd for

$K_2[WS_4]$ (%) **3**: WS_4, 79.97; Found: WS_4, 79.85%. IR data (cm^{-1}): 467 (ν_3). UV-Vis data are given in nm ($mol^{-1}\,L\,cm^{-1}$): 393 (10960), 278 (16350), 216 (20450).

2.5. *X-ray crystallography*

Intensity data for **1**–**3** were collected on an Image Plate Diffraction System from STOE using graphite-monochromated Mo-Kα radiation. The structures were solved with direct methods using SHELXS-97 [50] and refinement was done against F^2 using SHELXL-97 [50]. All non-hydrogen atoms were refined anisotropically. The hydrogens attached to the amine N in **1** and **2** were located in the difference map and refined isotropically using a riding model. The technical details of data acquisition and some selected crystal refinement results for **1**–**3** are summarized in table 2.

3. Results and discussion

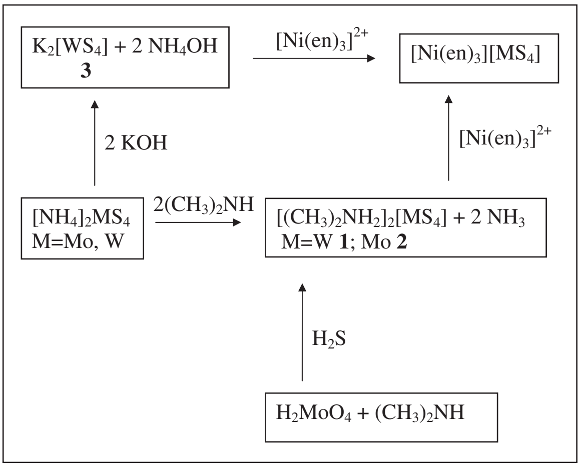
3.1. *Synthetic aspects*

The reaction of $(NH_4)_2[MS_4]$ with aqueous dimethylamine (scheme 1) followed by crystallization results in the formation of **1** or **2** in good yield. This synthetic methodology is very similar to the one employed by us for the synthesis of several organic tetrasulfidometalates. The reactivity characteristics of $[MS_4]^{2-}$ have been investigated with several organic reagents other than amines and $[MS_4]^{2-}$ can function as S-transfer reagents resulting in the formation of organo-sulfur compounds [14, 25]. The reaction of organic amines with $[MS_4]^{2-}$, designated as a base promoted cation exchange reaction in a very early report, differs from the reactions of $[MS_4]^{2-}$ with other organic substrates in which S-transfer takes place. In the base promoted cation exchange reaction, the stronger organic amine (pK_a of dimethylamine = 10.73) displaces the weaker ammonia (pK_a = 9.24) resulting in the exchange of ammonium cations in $(NH_4)_2[MS_4]$ by the organic ammonium cation. On reacting with amines, the tetrahedral $[MS_4]^{2-}$ core retains its identity resulting in the formation of organic tetrasulfidometalates. The reaction of $(NH_4)_2[MS_4]$ with aqueous dimethylamine forming **1** and **2** is in accordance with the known stability of $[MS_4]^{2-}$ in alkaline medium [16]. The reaction of KOH with $(NH_4)_2[WS_4]$ afforded the dipotassium salt of $[WS_4]^{2-}$ in good yields. The Mo analogue $K_2[MoS_4]$ was earlier synthesized by a solvothermal reaction of K_2S with MoO_3 in methanol [46]. $K_2[MoS_4]$ can also be prepared by the reaction of $(NH_4)_2[MoS_4]$ with KOH. For the synthesis of $K_2[MS_4]$, it is essential to warm the reaction mixture to expel the ammonia gas completely. K_2CO_3 can also be used as a base instead of KOH. In this case, the final product contains traces of ammonium as evidenced by a weak signal for N–H in the infrared spectrum.

Compound **2** can also be prepared by passing a rapid stream of H_2S into a solution of molybdic acid dissolved in 40% dimethylamine. It is well-documented [3, 4] that the reaction of an ammoniacal molybdate solution with H_2S results in the formation of $(NH_4)_2[MoS_4]$. Use of an organic amine in the above reaction instead of ammonia yields the organic tetrasulfidomolybdate **2**, which can be attributed to the initial formation of organic tetraoxomolybdate that further reacts with H_2S leading to the formation of an organic $[MoS_4]^{2-}$ compound.

Table 2. Crystal data and structure refinement for **1**–**3**.

Empirical formula	$[(CH_3)_2NH_2][WS_4]$ (**1**)	$[(CH_3)_2NH_2][MoS_4]$ (**2**)	$K_2[WS_4]$ (**3**)
Formula weight ($g\,mol^{-1}$)	404.28	316.37	390.29
Temperature (K)	170(2)	170(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	*Pnma*
Unit cell dimensions (Å, °)			
a	8.4639(6)	8.4529(5)	9.3437(7)
b	11.8598(6)	11.8339(8)	6.9310(4)
c	12.7419(8)	12.7011(7)	12.2143(7)
α	90	90	90
β	90.493(8)	90.594(7)	90
γ	90	90	90
Volume ($Å^3$), Z	1278.99(14), 4	1270.43(13), 4	791.01(9), 4
Calculated density ($mg\,m^{-3}$)	2.100	1.654	3.277
Absorption coefficient (mm^{-1})	9.640	1.645	16.600
$F(000)$	768	640	704
Crystal size (mm^3)	0.12 × 0.09 × 0.06	0.15 × 0.1 × 0.03	0.08 × 0.07 × 0.06
θ range for data collection (°)	2.35–28.09	2.35–28.03	2.74–29.22
Limiting Indices	$-11 \leq h \leq 11$; $-15 \leq k \leq 15$; $-16 \leq l \leq 16$	$-9 \leq h \leq 11$; $-14 \leq k \leq 15$; $-16 \leq l \leq 16$	$-12 \leq h \leq 12$; $-8 \leq k \leq 9$; $-16 \leq l$ d 16
Reflections collected	13,374	6671	12,924
Independent reflections	3074 [$(R_{int}) = (0.0287)$]	3040 [$(R_{int}) = (0.0297)$]	1142 [$(R_{int}) = (0.0876)$]
Completeness to theta = 25.02 (%)	98.6	99.1	98.7
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3074/0/104	3040/0/104	1142/0/41
Goodness-of-fit on F^2	1.033	0.977	1.362
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0246$, $wR_2 = 0.0622$	$R_1 = 0.0321$, $wR_2 = 0.0738$	$R_1 = 0.0276$, $wR_2 = 0.0559$
R indices (all data)	$R_1 = 0.0279$, $wR_2 = 0.0634$	$R_1 = 0.0437$, $wR_2 = 0.0776$	$R_1 = 0.0296$, $wR_2 = 0.0566$
Extinction coefficient	0.0058(3)	0.0119(8)	0.0059(5)
Largest difference peak and hole ($e \cdot Å^{-3}$)	1.779 and −1.243	1.057 and −0.995	0.981 and −0.972



Scheme 1. Synthesis of **1**–**3**.

All the compounds **1**–**3** 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 $[Ni(en)_3][MS_4]$ [22, 32]. Thus, the reaction of **1**–**3** with $[Ni(en)_3]^{2+}$ in 1 : 1 ratio leading to the formation of the insoluble $[Ni(en)_3][MS_4]$ constitutes a convenient method for the estimation of the $\%(MS_4)$ content in these compounds. All the compounds are soluble in water, aqueous ammonia, DMF and DMSO, but are insoluble in solvents such as CH_3CN or $CHCl_3$.

3.2. *Spectral studies*

Electronic spectra of **1** and **3** exhibit signals at 394, 279, and 217 nm which can be assigned to the intra-ligand charge transitions of $[WS_4]^{2-}$; the observed values are in good agreement with the data reported for $[WS_4]^{2-}$ [5, 6, 22–25]. The UV-Vis spectrum of **2** with signals at 469, 317, and 242 nm is characteristic of the red $[MoS_4]^{2-}$ chromophore [6, 24, 25].

Infrared spectra of **1** and **2** are nearly identical (Supplementary figure 1) with several signals observed in the mid-infrared spectra above 500 cm^{-1}. Based on a comparison of the IR spectra of **1** and **2** with that of $K_2[WS_4]$ which does not show any signal above 500 cm^{-1}, the signals observed above 500 cm^{-1} in **1** and **2** are attributed to the vibrations of the organic cation. These signals are also observed in the IR spectrum of dimethylammonium chloride (Supplementary figure 2), which does not show any signal below 500 cm^{-1}. Hence, the low-energy signals below 500 cm^{-1} are due to the vibrations of $[MS_4]^{2-}$. The N–H vibration of dimethylammonium chloride is slightly different from that of **1** or **2** due to the presence of Cl^-. For the free tetrahedral $[MS_4]^{2-}$, 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 [51]. The triply degenerate $\nu_3(F_2)$ asymmetric stretching M–S vibration is readily observed as an intense signal in all

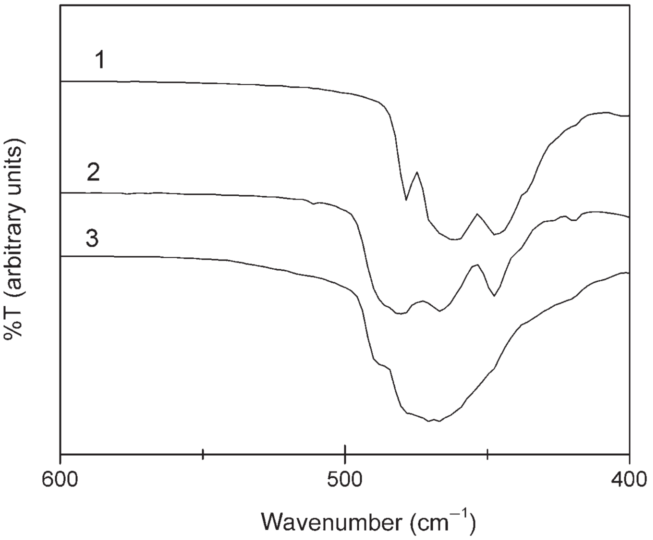


Figure 1. Infrared spectral trace of $[(CH_3)_2NH_2]_2[WS_4]$ **1**, $[(CH_3)_2NH_2]_2[MoS_4]$) **2**, and $K_2[WS_4]$ **3** in the M–S region.

$[MS_4]^{2-}$ compounds. When the tetrahedron is distorted the symmetry is slightly reduced, resulting in additional signals in the M–S region of the infrared spectrum, including the appearance of the symmetric stretching M–S vibration $\nu_1(A_1)$ as a signal of medium intensity [6, 23, 24]. In earlier reports we have shown that the distortion induces additional signals in the infrared spectrum when the difference between the longest and shortest M–S bond distances is more than 0.033 Å [31–34]. The infrared spectra of **1**–**3** in the lower energy region (figure 1) indicate that the $[MS_4]^{2-}$ tetrahedra in **1** and **2** are more distorted than **3**. The signals at 478 and 464 cm^{-1} in **1** are assigned to ν_1 and ν_3 vibrations, respectively, while signals at 480 and 467 cm^{-1} in **2** can be assigned to ν_3 and ν_1, respectively [5, 6, 31–34, 51]. In both **1** and **2** an additional signal at 447 cm^{-1} is observed. Compound **3** exhibits an intense signal at 466 cm^{-1} assignable for the triply degenerate $\nu_3(F_2)$ asymmetric stretching vibration, in agreement with the data reported for $Cs_2[WS_4]$ [43].

3.3. *Description of crystal structures of 1–3*

The bis(dimethylammonium) $[MS_4]^{2-}$ compounds **1** and **2** are isostructural and crystallize in the centrosymmetric monoclinic space group *P2$_1$/n* with all atoms situated in general positions. The crystal structure of **1** or **2** consists of a tetrahedral $[MS_4]^{2-}$ dianion (M=W **1**; M=Mo **2**) and two crystallographically independent dimethylammonium cations (figure 2). The geometric parameters of the organic cations in **1** and **2** are in the normal range (table 3). In **1**, the $[WS_4]^{2-}$ tetrahedron is slightly distorted and the S–W–S bond angles range between 108.77(4)° and 109.96(4)° (table 3). The W–S bond lengths vary from 2.1822(9) to 2.2176(9) Å with a mean value of 2.1958 Å. In the isostructural $[MoS_4]^{2-}$ compound, the Mo–S distances vary from 2.1776(8) to 2.2161(8) Å with a mean value of 2.1918 Å (table 3; Supplementary figure 3).

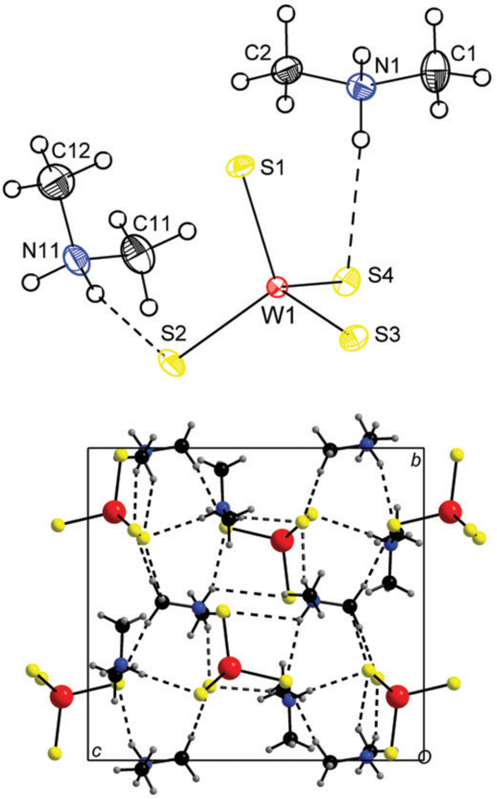


Figure 2. The crystal structure of $[(CH_3)_2NH_2]_2[WS_4]$ (**1**) showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown by broken lines (top). For the isostructural $[(CH_3)_2NH_2]_2[MoS_4]$ **2**, see "Supplementary material". The crystallographic packing of **1** viewed along *a*-axis. Hydrogen bonding interactions are shown as broken lines (bottom). Color code: W = red; S = yellow; C = black; N = blue; H = medium gray.

The difference Δ between the longest and shortest M–S bond distances is 0.0354 and 0.0385 Å for **1** and **2**, respectively, more than the observed Δ values for the alkali metal and methylammonium $[MS_4]^{2-}$ compounds listed in table 1. Based on the analysis of Δ values of several $[WS_4]^{2-}$ and $[MoS_4]^{2-}$ compounds, we have shown that for compounds with Δ larger than 0.033 Å the distortion of the $[MS_4]^{2-}$ tetrahedron shows up with the appearance of the ν_1 vibration as well as additional signals in the infrared spectrum [31–34] as observed in the IR spectra of **1** and **2**.

In **1**, the W1–S1 and W1–S2 distances are shorter than the mean W–S distance of 2.1958 Å, with the other two S atoms at longer distances indicating a distorted WS_4 tetrahedron. In **2**, a similar distribution of two long (Mo–S3 and Mo–S4) and two short Mo–S bonds is observed. The distribution of two short and two long M–S bonds in **1** and **2** can be attributed to weak hydrogen bonding interactions among $[MS_4]^{2-}$ and $[(CH_3)_2NH_2]^+$. The structure of **1** reveals a total of 10 weak hydrogen bonds comprising six N–H ··· S and four C–H ··· S interactions, the details of which are summarized in table 4. Thus, each $[WS_4]^{2-}$ is hydrogen bonded to eight different $[(CH_3)_2NH_2]^+$ cations (figure 3) with six N–H ··· S and four C–H ··· S interactions. One unique $[(CH_3)_2NH_2]^+$

Table 3. Selected bond lengths [Å] and bond angles [°].

[(CH$_3$)$_2$NH$_2$)]$_2$[WS$_4$] (**1**)			
W(1)–S(1)	2.1822(9)	N(1)–C(2)	1.477(6)
W(1)–S(2)	2.1866(10)	N(1)–C(1)	1.478(5)
W(1)–S(3)	2.1967(10)	N(11)–C(12)	1.478(6)
W(1)–S(4)	2.2176(9)	N(11)–C(11)	1.484(6)
S(1)–W(1)–S(2)	109.96(4)	S(1)–W(1)–S(4)	109.12(4)
S(1)–W(1)–S(3)	109.72(4)	S(2)–W(1)–S(4)	109.79(4)
S(2)–W(1)–S(3)	109.47(4)	S(3)–W(1)–S(4)	108.77(4)
C(2)–N(1)–C(1)	113.6(3)	C(12)–N(11)–C(11)	113.5(4)
[(CH$_3$)$_2$NH$_2$)]$_2$[MoS$_4$] (**2**)			
Mo(1)–S(2)	2.1776(8)	N(1)–C(1)	1.474(4)
Mo(1)–S(1)	2.1813(8)	N(1)–C(2)	1.483(4)
Mo(1)–S(4)	2.1922(7)	N(11)–C(12)	1.470(5)
Mo(1)–S(3)	2.2161(8)	N(11)–C(11)	1.488(5)
S(2)–Mo(1)–S(1)	109.98(3)	S(2)–Mo(1)–S(3)	109.16(3)
S(2)–Mo(1)–S(4)	109.70(3)	S(1)–Mo(1)–S(3)	109.76(3)
S(1)–Mo(1)–S(4)	109.43(3)	S(4)–Mo(1)–S(3)	108.79(3)
C(1)–N(1)–C(2)	113.7(3)	C(12)–N(11)–C(11)	114.3(3)
K$_2$[WS$_4$] **3**			
W(1)–S(3)	2.1758(13)	W(1)–S(2)	2.1776(16)
W(1)–S(3)^{i}	2.1758(13)	W(1)–S(1)	2.1901(16)
S(3)–W(1)–S(3)^{i}	107.74(7)	S(3)–W(1)–S(1)	109.99(5)
S(3)–W(1)–S(2)	108.88(5)	S(3)^{i}–W(1)–S(1)	109.99(5)
S(3)^{i}–W(1)–S(2)	108.88(5)	S(2)–W(1)–S(1)	111.27(7)

Symmetry transformations used to generate equivalent atoms: $^{i}[x, -y+3/2, z]$.

Table 4. Hydrogen-bonding geometry (Å, °) for [(CH$_3$)$_2$NH$_2$)]$_2$[WS$_4$] (**1**).

D–H···A	*d*(H···A)	*d*(D···A)	∠DHA	Symmetry code
N1–H1N···S4	2.386	3.256	158	$[x, y, z]$
N1–H2N···S3	2.397	3.243	153	$[-x+1, -y+1, -z+1]$
N1–H2N···S1	2.933	3.455	118	$[-x+1, -y+1, -z+1]$
N11–H3N···S4	2.435	3.283	153	$[x+1/2, -y+1/2, z+1/2]$
N11–H3N···S3	2.870	3.384	117	$[x+1/2, -y+1/2, z+1/2]$
N11–H4N···S2	2.380	3.282	167	$[x, y, z]$
C2–H2B···S3	2.807	3.769	167	$[x-1/2, -y+1/2, z+1/2]$
C2–H2C···S4	2.832	3.777	163	$[-x+1/2, y+1/2, -z+3/2]$
C2–H2A···S2	2.860	3.565	130	$[-x+3/2, y+1/2, -z+3/2]$
C1–H1A···S2	2.979	3.774	139	$[x-1, y, z]$

cation (N1) is hydrogen bonded to six different tetrasulfidotungstate anions via three N–H···S and four C–H···S bonds (figure 3). The second unique cation (N11) is hydrogen bonded to two different [WS$_4$]$^{2-}$ anions with the aid of three N–H···S interactions. A 3-D network of H-bonds is formed and a view of this network along the *a*-axis is displayed in figure 2. The S4 atom, which makes the longest W–S distance of 2.2176, is involved in two very short N–H···S bonds at 2.386 and 2.435 Å accounting for its elongation. In contrast, the S1 atom, which makes the shortest W–S bond distance of 2.1822(9), is involved in a bifurcated S···H contact at a longer distance of 2.933 Å accompanied by a N–H–S bond angle of 118°. The intermediate W–S bond lengths at 2.1866(10) and 2.1967(10) can be explained similarly. The Mo compound **2**

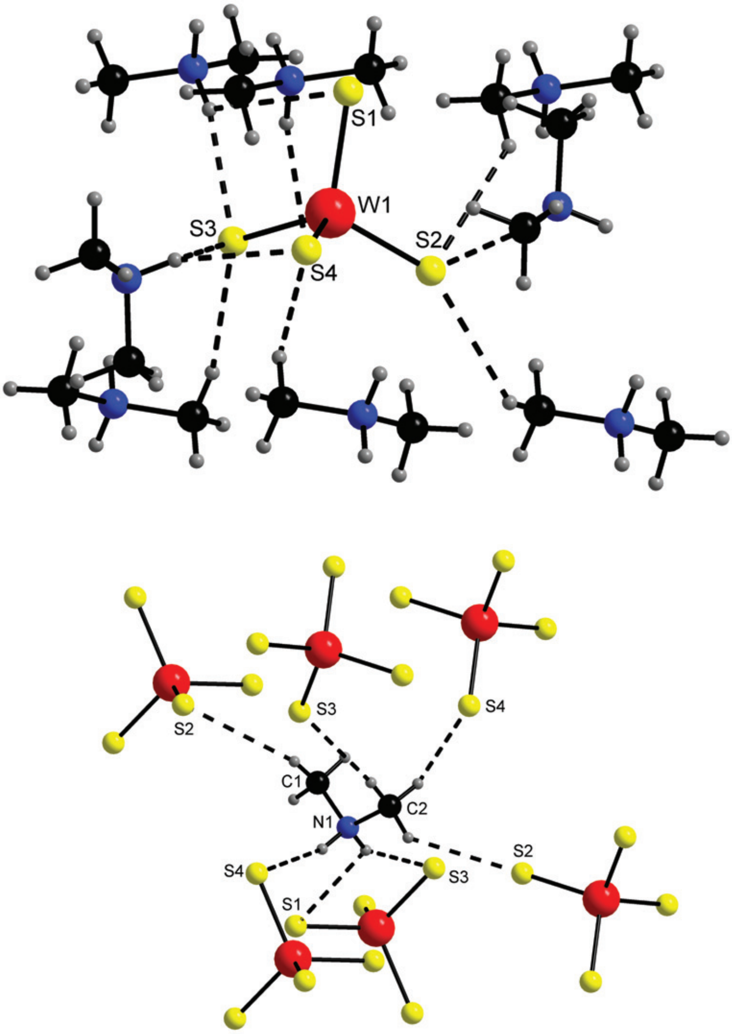


Figure 3. A view of the surroundings of the $[WS_4]^{2-}$ anion in **1** showing its linking to eight different $[(CH_3)_2NH_2]^+$ cations (top). A view of the surroundings of one of the unique organic cations in **1** showing the H-bonding situation (bottom). Color code: W = red; S = yellow; C = black; N = blue; H = medium gray.

exhibits identical H-bonding behavior (Supplementary figures 4 and 5) and the geometric parameters of the H-bonding interactions are listed in table 5.

Compound **3** crystallizes in the centrosymmetric orthorhombic space group *Pnma* and is isostructural with the ammonium and alkali metal tetrasulfidotungstates (table 1). The isostructural Mo compound, $K_2[MoS_4]$, was synthesized by a solvothermal method and its unit cell volume (770.49(13) Å^3) is about 20 Å^3 less than that of **3**. The structure of **3** consists of discrete slightly distorted tetrahedral $[WS_4]^{2-}$ of *m* symmetry, separated by two crystallographically independent K^+ situated on mirror planes (figure 4). In **3**, the S–W–S bond angles range between 107.74(7) and 111.27(7)° (table 3) while the W–S distances vary from 2.1758(13) to 2.1901(16) Å with a mean W–S bond length of 2.1798 Å (table 3). In view of the special position of the anion in **3**,

Table 5. Hydrogen-bonding geometry (Å,°) for $[(CH_3)_2NH_2)]_2[MoS_4]$ (**2**).

D–H···A	d(H···A)	d(D···A)	∠DHA	Symmetry code
N1–H1N···S4	2.391	3.237	153	$[-x+1, -y+1, -z+1]$
N1–H1N···S2	2.923	3.447	118	$[-x+1, -y+1, -z+1]$
N1–H2N···S3	2.382	3.252	158	$[x, y, z]$
N11–H3N···S3	2.413	3.268	155	$[x+1/2, -y+1/2, z+1/2]$
N11–H3N···S4	2.876	3.380	116	$[x+1/2, -y+1/2, z+1/2]$
N11–H4N···S1	2.387	3.287	166	$[x, y, z]$
C2–H2C···S3	2.811	3.756	162	$[-x+1/2, y+1/2, -z+3/2]$
C2–H2B···S4	2.810	3.771	167	$[x-1/2, -y+1/2, z+1/2]$
C1–H1A···S1	2.982	3.765	138	$[x-1, y, z]$
C2–H2A···S1	2.848	3.554	130	$[x-3/2, y+1/2, -z+3/2]$

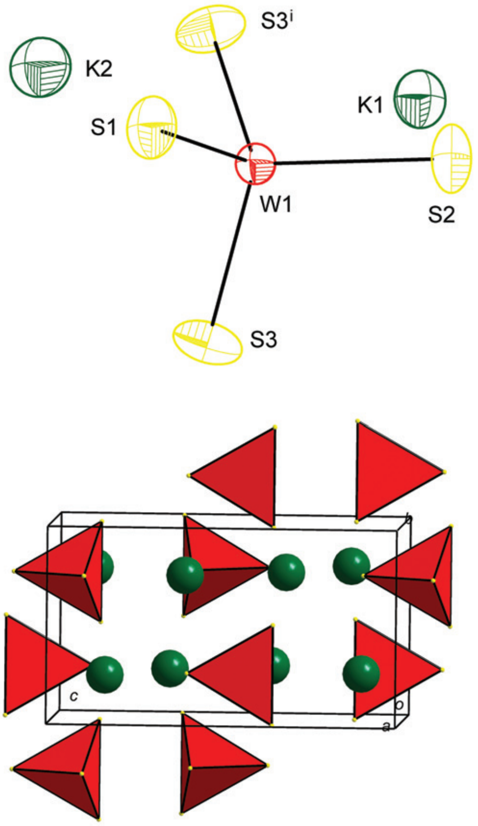


Figure 4. The crystal structure of $K_2[WS_4]$ (**3**) showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level (top). Color code: W = red; S = yellow; K = green. Symmetry code: $^i[x, -y+3/2, z]$. The crystallographic packing of $K_2[WS_4]$ **3** viewed along a-axis (bottom). $[WS_4]^{2-}$ units are represented as polyhedra.

two S atoms which lie on either side of a mirror plane are identical, resulting in two identical W–S distances at 2.1758(13) Å. This same structural feature is observed in all the alkali metal, ammonium, and methylammonium $[MS_4]^{2-}$ compounds, which exhibit two identical M–S distances. The crystallographic packing of **3** is displayed in figure 4.

Table 6. K···S distances in $K_2[WS_4]$ (**3**).

K(1)–S(2)	3.144(2)	K(2)–S(1)	3.355
K(1)–S(1)	3.358(2)	K(2)–S(3)^{ix}	3.4184(19)
K(1)–S(2)^{ii}	3.213(2)	K(2)–S(3)^{x}	3.4184(19)
K(1)–S(3)^{iii}	3.3272(18)	K(2)–S(2)^{xi}	3.5081(4)
K(1)–S(3)^{iv}	3.3272(18)	K(2)–S(2)^{xii}	3.5081(4)
K(1)–S(3)^{v}	3.4288(18)	K(2)–S(3)^{xiii}	3.527(2)
K(1)–S(3)^{vi}	3.4288(18)	K(2)–S(3)^{iv}	3.527(2)
K(1)–S(1)^{vii}	3.5556(6)	K(2)–S(1)^{xiv}	3.714(3)
K(1)–S(1)^{viii}	3.5556(6)		

Symmetry transformations used to generate equivalent atoms: $^{ii}x+1/2,\ -y+3/2,\ -z+1/2$; $^{iii}-x+1,\ y+1/2,\ -z+1$; $^{iv}x-1,\ -y+1,\ -z+1$; $^{v}-x+1/2,\ y+1/2,\ z-1/2$; $^{vi}-x+1/2,\ -y+1,\ z-1/2$; $^{vii}-x+1,\ y+1/2,\ -z+1$; $^{viii}-x+1,\ y-1/2,\ -z+1$; $^{ix}x+1,\ -y+3/2,\ z$; $^{x}x+1,\ y,\ z$; $^{xi}-x+1,\ y+1/2,\ -z+1$; $^{xii}-x+1,\ y-1/2,\ -z+1$; $^{xiii}-x+1/y+1/2,\ -z+1$; $^{xiv}x+1/2,\ -y+3/2,\ -z+3/2$.

The difference Δ between the longest and shortest W–S bond distance in **3** is 0.0143 Å, which is less than the Δ value of 0.0243 Å for $K_2[MoS_4]$ and much less than the observed Δ value for **1** and **2**. We note that the Δ values for alkali metal, ammonium, and methylammonium compounds are less than 0.0243 Å, except for $Rb_2[WS_4]$ which shows a Δ of 0.0343 Å (table 1). In **3**, the crystallographically independent K^+ cations are surrounded by several S atoms leading to irregular polyhedra. The K1–S bonds vary from 3.144(2) to 3.5556(6) Å while the K2–S distances range from 3.355(2) to 3.714(3) Å (table 6). K1 is linked to six symmetry-related $[WS_4]^{2-}$ tetrahedra via nine S atoms while K2 is surrounded by five symmetry-related $[WS_4]^{2-}$ tetrahedra via eight S atoms (Supplementary figure 6). The alkali metal tetrasulfidometalates exhibit several alkali metal···sulfur interactions while the methylammonium and dimethylamonium $[MS_4]^{2-}$ compounds show several N–H···S and C–H···S interactions.

4. Conclusions

In the present report, we have described the synthesis, spectral characteristics, and structural features of bis(dimethylammonium) tetrasulfidometalates and dipotassium tetrasulfidotungstate. A comparative study reveals the rich structural chemistry of these compounds.

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 no. CCDC 718848 (**1**) and CCDC 718847 (**2**). 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 or Email: deposit@ccdc.cam. .ac.uk). The crystallographic data of $K_2[WS_4]$ **3** is deposited with FIZ-Karlsruhe as CSD 420384 and can be obtained free of charge, on writing to FIZ, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-259), or Email: crysdata@fiz-karlsruhe.de. Additional figures related to the crystal structure and infrared spectra of **1**–**3** are available as supplementary data for this article and can be found in the online version.

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