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Synthesis and structural characterization of bis(dimethylammonium) tetrasulfidometalates

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Abstract

The reaction of $(\text{NH}_4)_2[\text{MS}_4]$ ($\text{M} = \text{Mo}, \text{W}$) with aqueous dimethylamine $(\text{CH}_3)_2\text{NH}$ or KOH results in the formation of bis(dimethylammonium) tetrasulfidometalates $[(\text{CH}_3)_2\text{NH}_2]_2[\text{MS}_4]$ ($\text{M} = \text{W}$ **1**; Mo **2**) or dipotassium tetrasulfidotungstate $\text{K}_2[\text{WS}_4]$ **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 $\text{P}2_1/\text{n}$. The structures consist of two crystallographically independent dimethylammonium cations and a slightly distorted tetrahedral $[\text{MS}_4]^{2-}$ anion with all atoms situated in general positions. The cations and anion are involved in several weak $\text{N-H}\cdots\text{S}$ and $\text{C-H}\cdots\text{S}$ interactions. Compound **3** crystallises in the centrosymmetric orthorhombic space group Pnma and is isostructural with the previously reported $\text{K}_2[\text{MoS}_4]$. The structure of **3** consists of discrete slightly distorted tetrahedral $[\text{WS}_4]^{2-}$ 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;

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1. Introduction

Recent reports on the use of $(\text{NH}_4)_2[\text{MS}_4]$ ($\text{M} = \text{Mo}, \text{W}$) 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 $[\text{MS}_4]^{2-}$ dianions are well known for their use as starting materials for the preparation of a variety of metal-sulfur compounds including catalytically important group VI metal sulfide materials [5-12]. The tetrasulfidometalates find use in therapy [13] and are employed as sulfur transfer reagents in organic synthesis [14]. As part of our research work 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 $[\text{MS}_4]^{2-}$ compounds stabilized by organic ammonium cations [19-24]. Our method involves the direct reaction of aqueous $(\text{NH}_4)_2[\text{MS}_4]$ with an organic amine and this work has resulted in the structural characterization of several new organic tetrasulfidometalates. Prior to our work, the reactions of tetraalkylammonium hydroxide with $[\text{MS}_4]^{2-}$ or tetraalkylammonium halide with $[\text{MS}_4]^{2-}$ in aqueous or non-aqueous media were shown to result in the formation of organic soluble $[\text{R}_4\text{N}]_2[\text{MS}_4]$ ($\text{R} = \text{alkyl}$) compounds [25-27].

The organic $[\text{MS}_4]^{2-}$ compounds exhibit several weak H-bonding interactions between the $[\text{MS}_4]^{2-}$ anion and the organic ammonium cation [19-24, 28-42]. These interactions (especially $\text{N-H}\cdots\text{S}$) 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 $[\text{MS}_4]^{2-}$ 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 $(\text{NH}_4)_2[\text{MS}_4]$ 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 $[\text{MS}_4]^{2-}$ compounds, shows that $(\text{NH}_4)_2[\text{MS}_4]$ compounds are isostructural with the corresponding alkali metal tetrasulfidometalates $(\text{M}')_2[\text{MS}_4]$ ($\text{M}' = \text{K}, \text{Rb}$ or Cs) [43-49] and bis(methylammonium) tetrasulfidometalates $[(\text{CH}_3)\text{NH}_3]_2[\text{MS}_4]$ [41-42] and crystallize in the centrosymmetric space group Pnma (Table 1). In this series of compounds the structure of $\text{K}_2[\text{WS}_4]$ has not been reported till date. In all these isostructural compounds the cations and $[\text{MS}_4]^{2-}$ anions are situated on mirror planes. Recently we reported on the group VI tetrasulfidometalates stabilized by methylammonium cation, which exhibit several $\text{C-H}\cdots\text{S}$ interactions in addition to $\text{N-H}\cdots\text{S}$ bonds [41-42]. In continuation of this work, it was of interest to investigate the reactions of $(\text{NH}_4)_2[\text{MS}_4]$ with dimethylamine $(\text{CH}_3)_2\text{NH}$. The results of these investigations and the synthesis and structure of $\text{K}_2[\text{WS}_4]$ are described in this paper

Table 1

2. Experimental

2.1 Materials and Methods

All the chemicals used in this study were of reagent grade and were 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) FT-IR spectrometer. UV-visible spectra were recorded on a Shimadzu UV-2450 double beam spectrophotometer using matched quartz cells.

2.2 Preparation of bis(dimethylammonium) tetrasulfidotungstate I

(NH₄)₂[WS₄] (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 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: 1.1g (95%)

Anal. Calc. for [(CH₃)₂NH₂]₂[WS₄] **1**: C 11.88; H, 3.99; N, 6.93; WS₄ 77.20; Found: C, 11.85; H, 3.88; N, 6.77; WS₄, 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 (ν₁), 461 (ν₃), 448

UV-Vis data in nm (mol⁻¹.L. cm⁻¹): 394 (17105), 279 (25290), 217 (30890).

2.2 Preparation of bis(dimethylammonium) tetrasulfidomolybdate **2**

The reaction of freshly prepared (NH₄)₂[MoS₄] (1.04 g, 4 mmol) instead of (NH₄)₂[WS₄] 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 MoO₃. 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 H₂S gas was passed for 40 minutes by maintaining the reaction mixture at ~ 60°C. When red solid material started appearing, the gas flow was stopped, the flask 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, which were isolated as before.

Total yield ~5.7 g (97%)

Anal. Calc. for $[(\text{CH}_3)_2\text{NH}_2]_2[\text{MoS}_4]$ **2**: C, 15.18; H, 5.10; N, 8.85; S, 40.54; MoS₄, 70.86; Found: C, 15.10; H, 5.07; N, 8.17; MoS₄, 70.09 %.

IR data (cm^{-1}): 3021 ($\nu_{\text{N-H}}$), 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 in nm ($\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$): 469 (12210), 317 (16600), 242 (23620)

2.2 Preparation of dipotassium tetrasulfidotungstate **3**

$(\text{NH}_4)_2[\text{WS}_4]$ (348 mg, 1 mmol) was dissolved in water (8 mL) containing KOH (112 mg, 2mmol). The clear yellow solution thus obtained was warmed on a water bath at ~60 °C for 15-20 minutes 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** that had separated were isolated by using a similar procedure mentioned earlier for **1**.

Anal. Calc. for $\text{K}_2[\text{WS}_4]$ **3**: WS₄, 79.97; Found: WS₄, 79.85 %.

IR data (cm^{-1}): 467 (ν_3)

UV-Vis data in nm ($\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$): 393 (10960), 278 (16350), 216 (20450)

2.3 X-ray crystallography

Intensity data for compounds **1-3** were collected on an Image Plate Diffraction System from STOE using graphite-monochromated Mo- K_α radiation. The structure was 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 hydrogen atoms attached to the amine N in **1** and **2** were located

in the difference map and were refined isotropically using a riding model. The technical details of data acquisition and some selected crystal refinement results for compounds **1-3** are summarized in [Table 2](#).

< [Table 2](#) >

3. Results and Discussion

3.1 Synthetic aspects

The reaction of $(\text{NH}_4)_2[\text{MS}_4]$ with aqueous dimethylamine ([Scheme 1](#)) followed by crystallization, results in the formation of **1** or **2** in good yields. This synthetic methodology is very similar to the one employed by us for the synthesis of several organic tetrasulfidometalates. It is to be noted that the reactivity characteristics of the tetrahedral $[\text{MS}_4]^{2-}$ has been investigated with several organic reagents other than amines and it has been shown that $[\text{MS}_4]^{2-}$ can function as S-transfer reagents resulting in the formation of novel organo-sulfur compounds [14, 25]. The reaction of organic amines with $[\text{MS}_4]^{2-}$, designated by us as a base promoted cation exchange reaction in a very early report, differs from the reactions of $[\text{MS}_4]^{2-}$ with other organic substrates in that no S-transfer takes place. In the base promoted cation exchange reaction, the stronger organic amine (pKa of dimethylamine = 10.73) displaces the weaker ammonia (pKa = 9.24) resulting in the exchange of ammonium cations in $(\text{NH}_4)_2[\text{MS}_4]$ by the organic ammonium cation for charge balance. Further it is to be noted that on reacting with amines, the tetrahedral $[\text{MS}_4]^{2-}$ core retains its identity resulting in the formation of organic tetrasulfidometalates. The reaction of $(\text{NH}_4)_2[\text{MS}_4]$ with aqueous dimethylamine to form the new compounds **1** and **2** is in accordance with the known stability of $[\text{MS}_4]^{2-}$ in alkaline medium [16]. The reaction of KOH with $(\text{NH}_4)_2[\text{WS}_4]$ afforded the dipotassium salt of $[\text{WS}_4]^{2-}$ in good yields. The Mo analogue $\text{K}_2[\text{MoS}_4]$ has earlier been 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 so as to expel the ammonia gas completely. K_2CO_3 can also be used as a base instead of KOH . In this case it is noted that 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 gas 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 $(NH_4)_2[MoS_4]$. The use of an organic amine in the above reaction instead of ammonia affords the organic tetrasulfidomolybdate compound **2**, which can be attributed to the initial formation of organic tetraoxomolybdate which further reacts with H_2S leading to the formation of an organic $[MoS_4]^{2-}$ compound.

All the compounds (**1** to **3**) which are crystallized from a strongly alkaline medium 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 all these compounds. All the compounds are soluble in water, aqueous ammonia, DMF and DMSO but are insoluble in organic solvents such as CH_3CN or $CHCl_3$.

3.2 Spectral studies

The electronic spectra of the W containing tetrasulfidometalates **1** and **3** exhibit signals at around 394, 279 and 217 nm which can be assigned to the intra-ligand

charge transitions of the $[\text{WS}_4]^{2-}$ moiety and the observed values are in very good agreement with the reported data for $[\text{WS}_4]^{2-}$ chromophore [5, 6, 22-25]. The UV-Vis spectrum of **2** with signals at 469, 317, 242 nm is characteristic of the red $[\text{MoS}_4]^{2-}$ chromophore [6, 24-25].

The infrared spectra of the organic tetrasulfidometalates **1** and **2** are nearly identical (Supplementary Figure 1) and several signals are observed in the mid-infrared spectra above 500 cm^{-1} . Based on a comparison of the IR spectra of compounds **1** and **2** with that of $\text{K}_2[\text{WS}_4]$ which does not show any signal above 500 cm^{-1} , the signals observed above 500 cm^{-1} in **1** and **2** can be attributed to the vibrations of the organic cation. Interestingly all of these signals also are observed in the IR spectrum of dimethylammonium chloride (Supplementary Figure 2) which does not show any signal in the region below 500 cm^{-1} . Hence, the low energy signals below 500 cm^{-1} are due to the vibrations of the $[\text{MS}_4]^{2-}$ moiety. It is to be noted that the profile of the N-H vibration of dimethylammonium chloride is slightly different from that of **1** or **2** due to the presence of Cl^- counter anion. For the free tetrahedral $[\text{MS}_4]^{2-}$ anion four characteristic vibrations $\nu_1(\text{A}_1)$, $\nu_2(\text{E})$, $\nu_3(\text{F}_2)$ and $\nu_4(\text{F}_2)$ are expected, all of which are Raman active while only ν_3 and ν_4 are IR active [51]. The triply degenerate $\nu_3(\text{F}_2)$ asymmetric stretching M-S vibration is readily observed as an intense signal in all $[\text{MS}_4]^{2-}$ 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 $\nu_1(\text{A}_1)$ 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 \AA [31-34] A scrutiny of the infrared spectra of the compounds **1-3** in the lower energy region (figure 1)

indicates that the $[\text{MS}_4]^{2-}$ tetrahedra in compounds **1** and **2** are more distorted as compared to that in **3**. The signals at 478 and 464 cm^{-1} in **1** can be assigned to the ν_1 and ν_3 vibrations respectively while the signals at 480 and 467 cm^{-1} in compound **2** can be assigned to the ν_3 and ν_1 vibrations respectively [5,6, 31-34, 51]. In both **1** and **2** an additional signal at around 447 cm^{-1} is observed. Compound **3** exhibits an intense signal at 466 cm^{-1} assignable for the triply degenerate $\nu_3(\text{F}_2)$ asymmetric stretching vibration, which is in agreement with the reported data for $\text{Cs}_2[\text{WS}_4]$ [43].

< Figure 1 >

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

The bis(dimethylammonium) $[\text{MS}_4]^{2-}$ compounds **1** and **2** are isostructural and crystallize in the centrosymmetric monoclinic space group $\text{P2}_1/\text{n}$ with all atoms situated in general positions. The crystal structure of **1** or **2** consists of a tetrahedral $[\text{MS}_4]^{2-}$ 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 compound **1** the $[\text{WS}_4]^{2-}$ tetrahedron is slightly distorted and the S–W–S bond angles range between 108.77(4) and 109.96(4) $^\circ$ (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 $[\text{MoS}_4]^{2-}$ 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). The difference Δ between the longest and shortest M–S bond distances is 0.0354 and 0.0385 Å for compounds **1** and **2** respectively. Interestingly the Δ values for compounds **1** and **2** are more than the observed Δ values for the alkali metal and methylammonium $[\text{MS}_4]^{2-}$ compounds listed in Table 1. Based on an analysis of Δ values of several $[\text{WS}_4]^{2-}$ and $[\text{MoS}_4]^{2-}$ compounds we have shown that for compounds with Δ larger than 0.033 Å the distortion of the $[\text{MS}_4]^{2-}$

tetrahedron shows up in the form of 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 compounds **1** and **2**.

< Table 3 Figure 2 >

In compound **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 WS₄ tetrahedron. In compound **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 compounds **1** and **2** can be attributed to the several weak hydrogen bonding interactions observed among the [MS₄]²⁻ anions, and the [(CH₃)₂NH₂]⁺ organic cations. A scrutiny of the structure of **1** reveals a total of ten weak hydrogen bonds comprising of six N-H...S, and four C-H...S interactions the details of which are summarized in Table 4. Thus each [WS₄]²⁻ ion is hydrogen bonded to eight different [(CH₃)₂NH₂]⁺ cations (figure 3) with the aid of six N-H...S and four C-H...S interactions. One unique [(CH₃)₂NH₂]⁺ 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 [WS₄]²⁻ anions with the aid of three N-H...S interactions. As a result of H-bonding, a three dimensional network of H-bonds is formed and a view of this network along the *a* axis is displayed in figure 2. An analysis of the several H-bonds also reveals that 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 NHS bond angle of 118°. The intermediate W-S bond lengths at

2.1866(10) and 2.1967(10) can be explained similarly. The isotypic Mo compound **2** exhibits an identical H-bonding behavior ([Supplementary Figures 4-5](#)) and the geometric parameters of the H-bonding interactions are listed in [Table 5](#).

< [Figure 3](#); [Table 4, 5](#) >

Compound **3** crystallizes in the centrosymmetric orthorhombic space group Pnma and is isostructural with the ammonium and alkali metal tetrasulfidtungstates ([Table 1](#)). The isostructural Mo compound $K_2[MoS_4]$ was synthesized by a solvothermal method and its unit cell volume ($770.49(13) \text{ \AA}^3$) is about 20 \AA^3 less than that of **3**. The structure of **3** consists of discrete slightly distorted tetrahedral $[WS_4]^{2-}$ anions of m symmetry, separated by two crystallographically independent K^+ cations situated on mirror planes ([figure 4](#)). In **3** the S–W–S bond angles range between $107.74(7)$ and $111.27(7)^\circ$ ([Table 3](#)) while the W–S distances vary from $2.1758(13)$ to $2.1901(16) \text{ \AA}$ with a mean W–S bond length of 2.1798 \AA ([Table 3](#)). In view of the special position of the anion in **3**, two S atoms which lie on either side of a mirror plane are identical resulting in two identical W–S distances at $2.1758(13) \text{ \AA}$. 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. A view of the crystallographic packing of **3** is displayed in [figure 4](#). The difference Δ between the longest and shortest W–S bond distance in **3** is 0.0143 \AA which is less than the Δ value of 0.0243 \AA for $K_2[MoS_4]$ and much less than the observed Δ value for the bis(dimethylammonium) $[MS_4]^{2-}$ compounds **1** and **2**. We note that the Δ values for the alkali metal, ammonium and methylammonium compounds are less than 0.0243 \AA excepting for $Rb_2[WS_4]$ which shows a Δ of 0.0343 \AA ([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 $3.5556(6) \text{ \AA}$

while the K2-S distances range from 3.355(2) to 3.714(3) Å (Table 6). K1 is linked to six symmetry related $[\text{WS}_4]^{2-}$ tetrahedra via nine S atoms while K2 is surrounded by five symmetry related $[\text{WS}_4]^{2-}$ tetrahedra via eight S atoms (Supplementary Figure 6). The alkali metal tetrasulfidometalates exhibit several alkali metal...sulfur interactions while the methylammonium and dimethylammonium $[\text{MS}_4]^{2-}$ compounds show several N-H...S and C-H...S interactions.

< Figure 4 and Table 6 >

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 paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 718848 (1), 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 $\text{K}_2[\text{WS}_4]$ 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 compounds 1-3, are available as

Supplementary data for this article and can be found in the online version *****.

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

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 \cdots S	46
(K) ₂ [WS ₄]	Pnma	2.1901	2.1758	0.0143	K \cdots S	This Work
Rb ₂ [WS ₄]	Pnma	2.2053	2.1710	0.0343	Rb \cdots S	47
Rb ₂ [MoS ₄]	Pnma	2.1917	2.1782	0.0135	Rb \cdots S	48
Cs ₂ [WS ₄]	Pnma	2.2079	2.1915	0.0164	Cs \cdots S	43
Cs ₂ [MoS ₄]	Pnma	2.1935	2.1809	0.0126	Cs \cdots S	49
(NH ₄) ₂ [WS ₄]	Pnma	2.2090	2.1856	0.0234	N-H \cdots S	44
(NH ₄) ₂ [MoS ₄]	Pnma	2.186	2.171	0.015	N-H \cdots S	45
(CH ₃ NH ₃) ₂ [WS ₄]	Pnma	2.2010	2.1862	0.0148	N-H \cdots S, C-H \cdots S	41
(CH ₃ NH ₃) ₂ [MoS ₄]	Pnma	2.1961	2.1762	0.0199	N-H \cdots S, C-H \cdots S	42
[(CH ₃) ₂ NH ₂] ₂ [WS ₄]	P2 ₁ /n	2.2176	2.1822	0.0354	N-H \cdots S, C-H \cdots S	This Work
[(CH ₃) ₂ NH ₂] ₂ [MS ₄]	P2 ₁ /n	2.2161	2.1776	0.0385	N-H \cdots S, C-H \cdots S	This Work

Table 2 — Crystal data and structure refinement for compounds **1-3**

Empirical formula	$[(\text{CH}_3)_2\text{NH}_2][\text{WS}_4]$ 1	$[(\text{CH}_3)_2\text{NH}_2][\text{MoS}_4]$ 2	$\text{K}_2[\text{WS}_4]$ 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	$\text{P2}_1/\text{n}$	$\text{P2}_1/\text{n}$	Pnma
a (Å)	8.4639(6)	8.4529(5)	9.3437(7)
b (Å)	11.8598(6)	11.8339(8)	6.9310(4)
c (Å)	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)	1278.99(14)	1270.43(13)	791.01(9)
Z	4	4	4
D_{calc} (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 x 0.09 x 0.06	0.15 x 0.1 x 0.03	0.08 x 0.07 x 0.06
Θ range for data collection (°)	2.35 to 28.09	2.35 to 28.03	2.74 to 29.22
Index ranges	$-11 \leq h \leq 11, -15 \leq k \leq 15,$ $-16 \leq l \leq 16$	$-9 \leq h \leq 11, -14 \leq k \leq 15,$ $-16 \leq l \leq 16$	$-12 \leq h \leq 12, -8 \leq k \leq 9,$ $-16 \leq l \leq 16$
Reflections collected	13374	6671	12924
Independent reflections (R_{int})	3074 (0.0287)	3040 (0.0297)	1142 (0.0876)
Completeness to theta	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 [$I > 2\sigma(I)$]	$R1 = 0.0246,$ $wR2 = 0.0622$	$R1 = 0.0321,$ $wR2 = 0.0738$	$R1 = 0.0276,$ $wR2 = 0.0559$
R indices (all data)	$R1 = 0.0279,$ $wR2 = 0.0634$	$R1 = 0.0437,$ $wR2 = 0.0776$	$R1 = 0.0296,$ $wR2 = 0.0566$
Extinction coefficient	0.0058(3)	0.0119(8)	0.0059(5)
Largest difference peak and hole (e.Å^{-3})	1.779 and -1.243	1.057 and -0.995	0.981 and -0.972

Table 3. Selected bond lengths [\AA] and bond angles [$^\circ$].

$[(\text{CH}_3)_2\text{NH}_2]_2[\text{WS}_4]$ **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)

$[(\text{CH}_3)_2\text{NH}_2]_2[\text{MoS}_4]$ **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)

$\text{K}_2[\text{WS}_4]$ **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 (\AA , $^\circ$) for $[(\text{CH}_3)_2\text{NH}_2]_2[\text{WS}_4]$ **1**

D-H...A	$d(\text{H}\cdots\text{A})$	$D(\text{D}\cdots\text{A})$	$\angle\text{DHA}$	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]

Table 5 Hydrogen-bonding geometry (\AA , $^\circ$) for $[(\text{CH}_3)_2\text{NH}_2]_2[\text{MoS}_4]$ **2**

D-H...A	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle\text{DHA}$	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]

Table 6. K...S distances in K₂[WS₄] **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) $-x+1/2, y+1/2, -z+1$;
xiv) $x+1/2, -y+3/2, -z+3/2$;

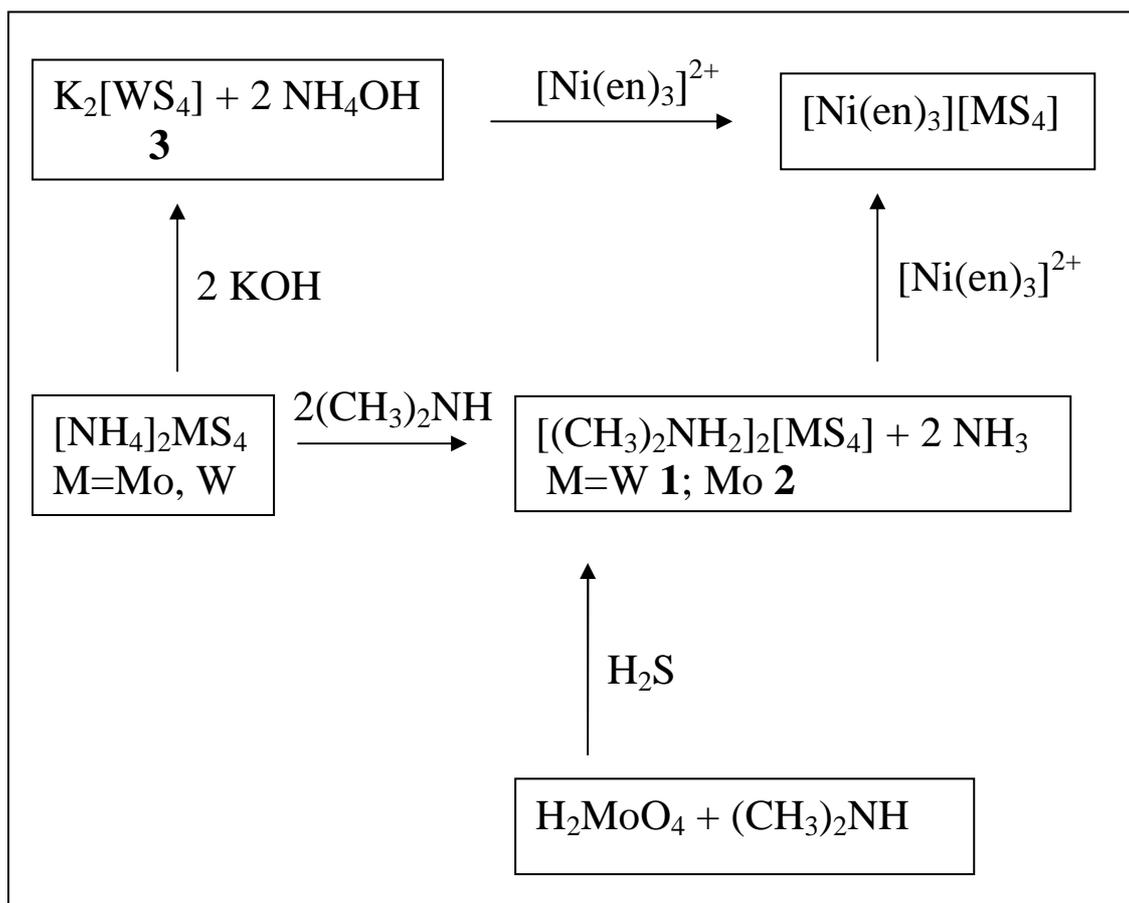
Caption for Figures:

Fig.1. Infrared spectral trace of $((\text{CH}_3)_2\text{NH}_2)_2[\text{WS}_4]$ **1**, $((\text{CH}_3)_2\text{NH}_2)_2[\text{MoS}_4]$ **2** and $\text{K}_2[\text{WS}_4]$ **3** in the M-S region.

Figure 2 The crystal structure of $[(\text{CH}_3)_2\text{NH}_2]_2[\text{WS}_4]$ **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 $[(\text{CH}_3)_2\text{NH}_2]_2[\text{MoS}_4]$ **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 grey.

Figure 3: A view of the surroundings of the $[\text{WS}_4]^{2-}$ anion in **1** showing its linking to eight different $[(\text{CH}_3)_2\text{NH}_2]^+$ 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 grey.

Figure 4 The crystal structure of $\text{K}_2[\text{WS}_4]$ **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 $\text{K}_2[\text{WS}_4]$ **3** viewed along a axis. (bottom). $[\text{WS}_4]^{2-}$ units are represented as polyhedra.



Scheme 1

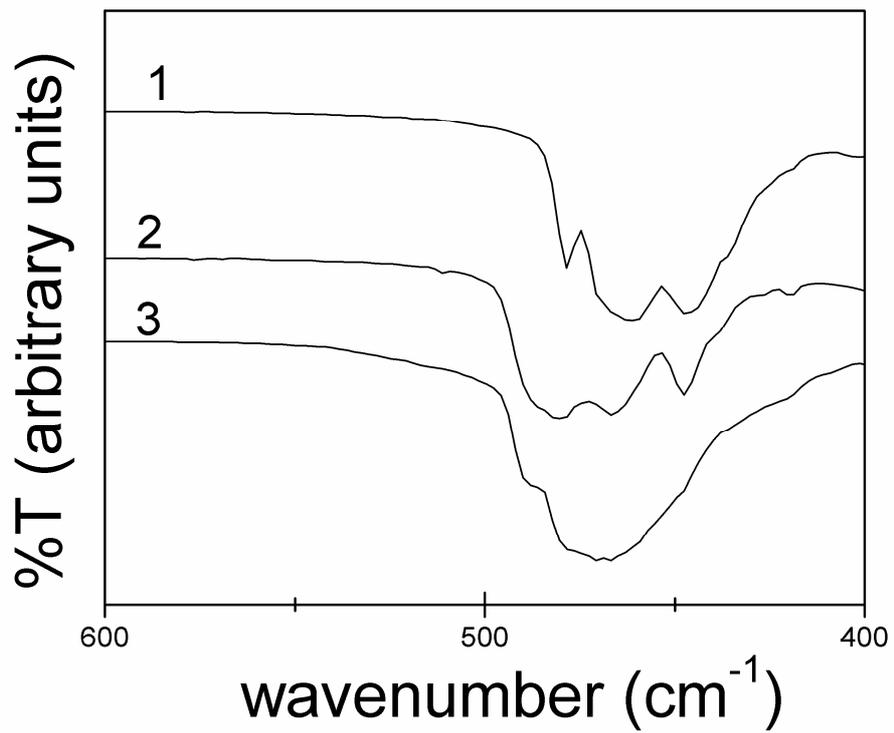


Fig.1. Infrared spectral trace of [(CH₃)₂NH₂]₂[WS₄] **1**, [(CH₃)₂NH₂]₂[MoS₄] **2** and K₂[WS₄] **3** in the M-S region.

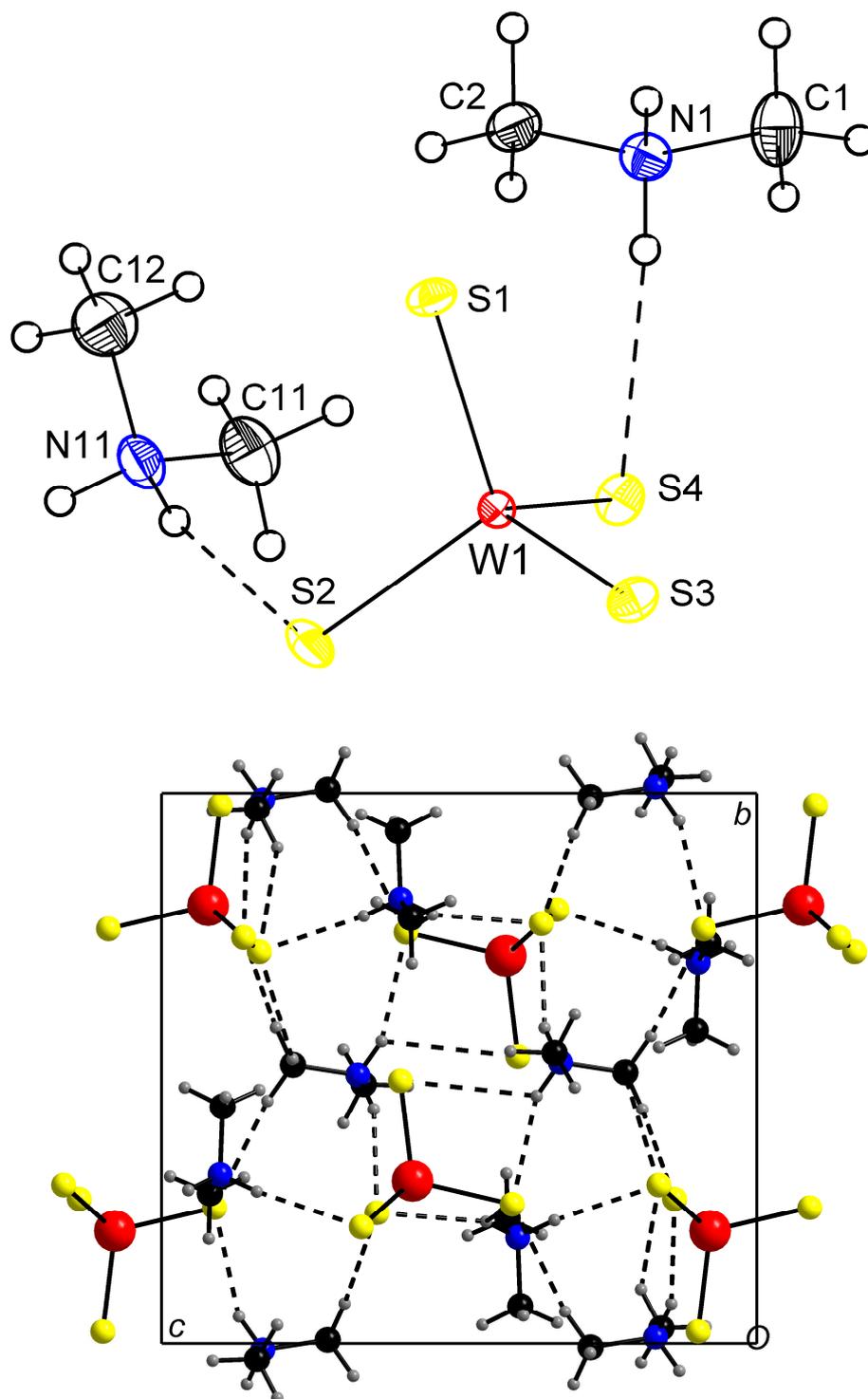


Fig. 2 The crystal structure of $[(\text{CH}_3)_2\text{NH}_2]_2[\text{WS}_4]$ **1** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown by broken lines (top). For the isostructural $[(\text{CH}_3)_2\text{NH}_2]_2[\text{MoS}_4]$ **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 grey.

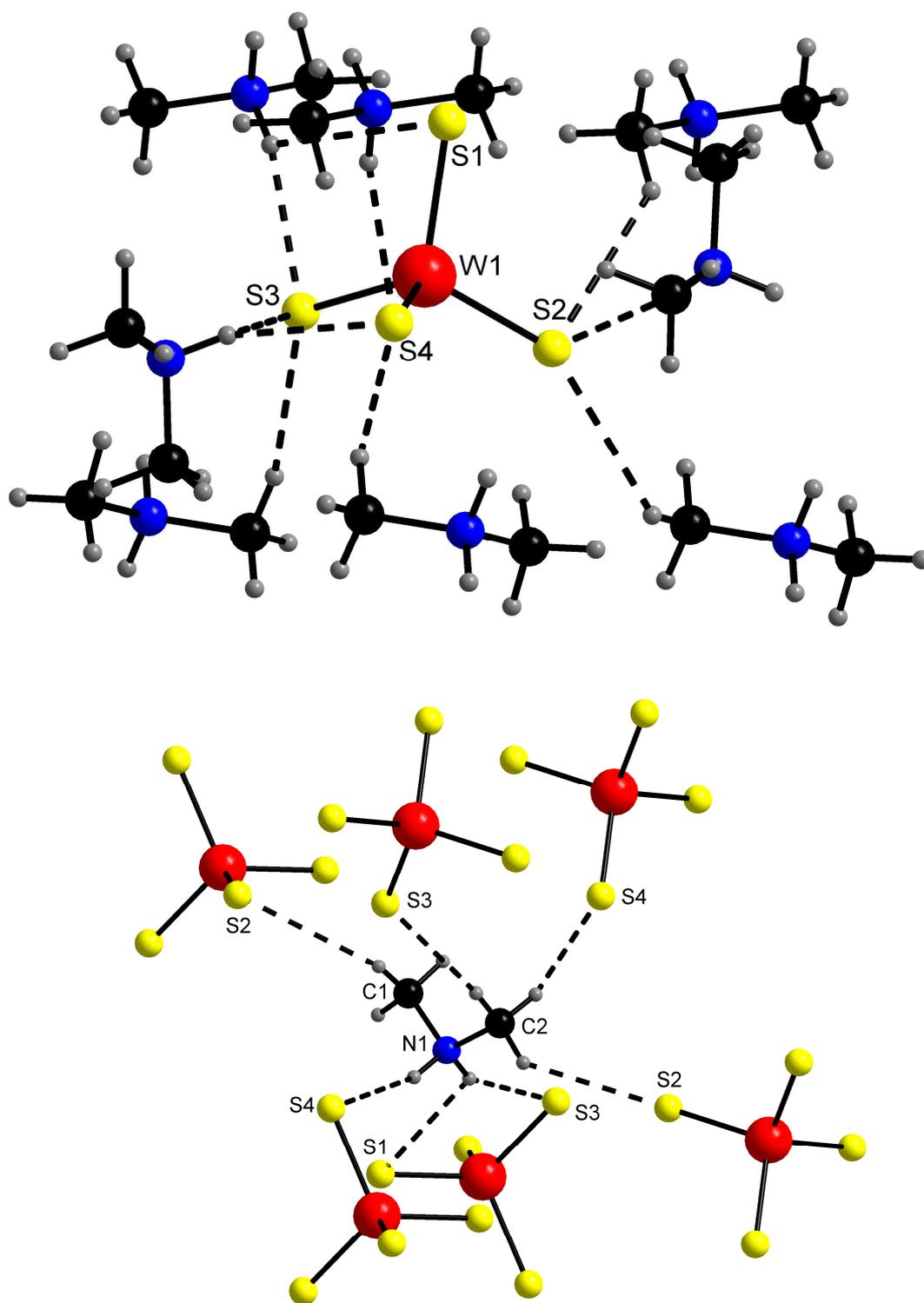


Fig. 3: A view of the surroundings of the $[WS_4]^{2-}$ anion in **1** showing its linking to eight different $[(CH_3)_2NH_2]^+$ cations (top). A view of the surroundings of one of the unique organic cations in **1** showing the H-bonding situation (bottom) Color code: W=red; S=yellow; C=black; N=blue;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

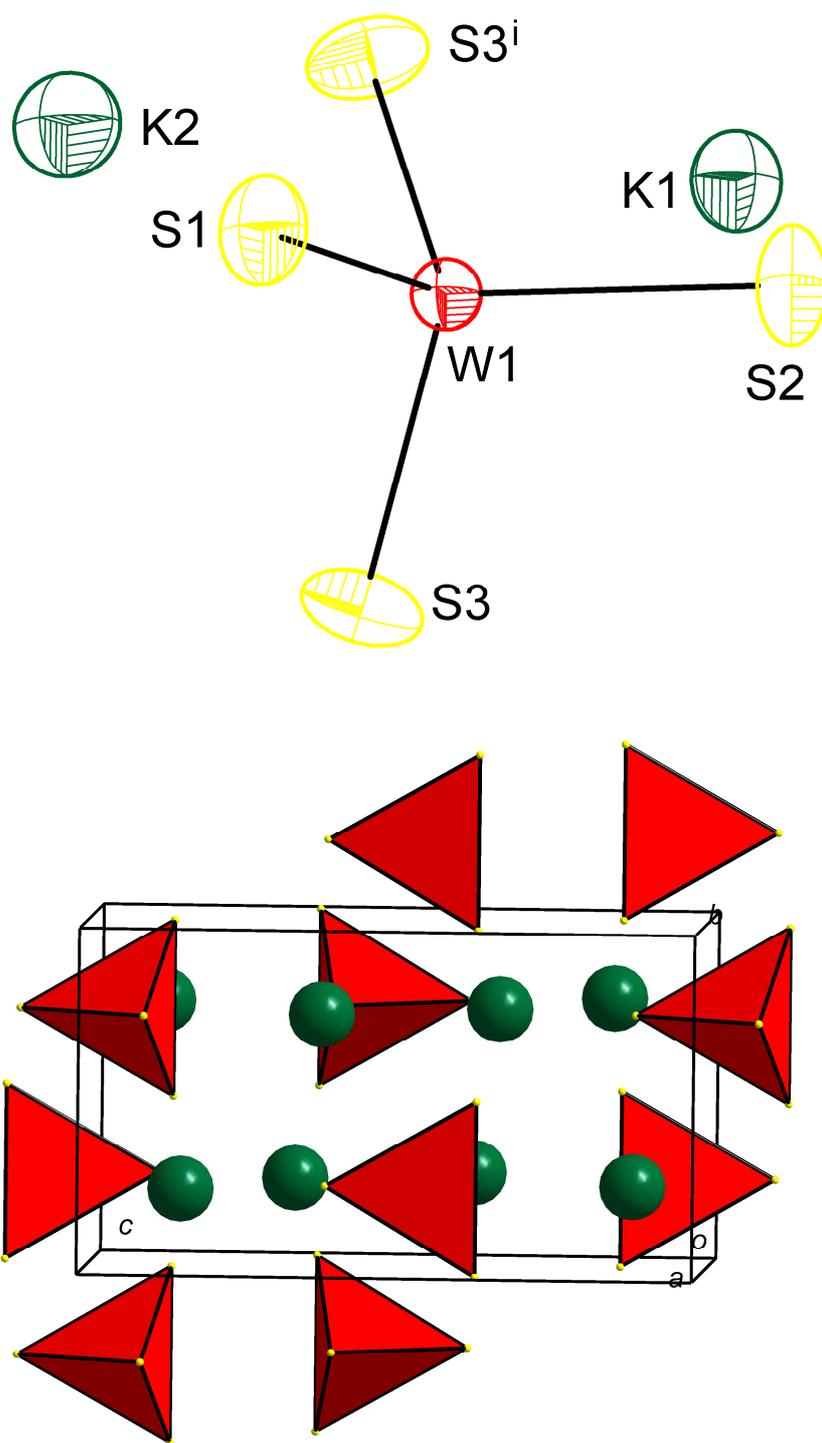


Fig. 4 The crystal structure of $K_2[WS_4]$ **3** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. (top). Color code: W=red; S=yellow; K=green. Symmetry code : *i*) $[x, -y+3/2, z]$. The crystallographic packing of $K_2[WS_4]$ **3** viewed along *a* axis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