Synthesis and structural characterization of bis(*n*-propylammonium) tetrasulfidometalates

Bikshandarkoil R Srinivasan[a,*], Ashish R Naik[a], Christian Näther[b] & Wolfgang Bensch[b]

[a]Department of Chemistry, Goa University, Goa 403 206, India
Email: srini@unigoa.ac.in
[b]Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Max-Eyth Straße 2, D-24118, Kiel, Germany

The reaction of $(NH_4)_2[MS_4]$ (M = W, Mo) with *n*-propylamine (CH_3-CH_2-CH_2-NH_2) results in the formation of bis(*n*-propylammonium) tetrasulfidometalates $(CH_3$-CH_2-CH_2-$NH_3)_2[MS_4]$ (M = W (**1**); Mo (**2**)). Both compounds have been characterized by elemental analysis, IR, Raman and UV-vis spectra and crystal structures. Compounds (**1**) and (**2**) are isostructural and crystallize in the centrosymmetric orthorhombic space group, P*nma*. The structure consists of discrete slightly distorted tetrahedral tetrasulfidometalate $[MS_4]^{2-}$ anions of *m* symmetry, separated by two crystallographically independent *n*-propylammonium cations located on mirror planes. The carbon atoms of the organic cations are disordered. A comparative study of twelve tetrasulfidometalates crystallizing in the orthorhombic space group P*nma* is presented.

Recent reports by Jakobsen *et al.*[1,2] on the use of $(NH_4)_2[MS_4]$ (M = Mo, W) for advancements in natural abundance solid state ^{33}S MAS NMR spectroscopy have added an entire new dimension to the chemistry of these well known compounds. The tetrasulfidometalates $[MS_4]^{2-}$ have been investigated by several research groups in the last three decades[3-7] and have been reported to be able to function as sulfur transfer reagents in organic synthesis[8]. As part of our research program[9-12] we have been investigating the synthesis, spectral characteristics and thermal properties of group VI tetrasulfidometalates. We have demonstrated that the direct reaction of aqueous $(NH_4)_2[MS_4]$ with an organic amine constitutes a convenient and general method for the facile synthesis of crystalline $[MS_4]^{2-}$ compounds stabilized by organic ammonium cations[13-18]. Prior to our work, the 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[19-21].

The flexibility of the $[MS_4]^{2-}$ moiety to exist in different structural environments can be evidenced by its characterization with several organic ammonium counter cations[14-20]. The organic $[MS_4]^{2-}$ compounds exhibit several weak H-bonding interactions between the $[MS_4]^{2-}$ anion and the organic cations, which can be tuned by varying the steric bulk as well as the number of potential donor H atoms on the amine N atom. We have earlier investigated the reactions of $(NH_4)_2[MS_4]$ with several acyclic and cyclic di-, tri- and tetra-amines. Herein, we describe the synthesis and characterization of two new tetrasulfidometalates stabilized by *n*-propylammonium cation.

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 literature procedure[21]. Far-IR spectra (range 80 to 500 cm^{-1}) were recorded using a Bruker IFS 66 infrared spectrometer in pressed polyethylene disks. Mid-infrared spectra were collected in a KBr matrix using a Shimadzu (IR Prestige-21) FT-IR spectrometer and a ATI Mattson Genesis infrared spectrometer in the range 4000-400 cm^{-1}. Raman spectra were recorded in the region 100-3500 cm^{-1} on a Bruker FRA 106 Fourier Transform Raman

spectrometer. UV-visible spectra were obtained using a Shimadzu UV-2450 double beam spectrophotometer using matched quartz cells. The $[MS_4]^{2-}$ content of (**1**) and (**2**) was estimated as the insoluble $[Ni(en)_3][MS_4]$ as described earlier[11,16]

Synthesis of bis(*n*-propylammonium) tetrasulfidotungstate (1)

$(NH_4)_2[WS_4]$ (348 mg, 1 mmol) was dissolved in water (~15 mL) and ~ 7 drops of *n*-propylamine was added. The reaction mixture was filtered and the filtrate was left aside for crystallization resulting in the formation of yellow blocks of (**1**). The crystalline product was filtered, washed with a little ice-cold water followed by 2-propanol and dried in air to obtain (1) in 45% yield.

Anal.: Calc. for $C_6H_{20}N_2S_4W$ (**1**): C 16.67; H, 4.66; N, 6.48; S, 29.67; WS_4 72.19; Found: C, 16.85; H, 4.63; N, 6.71; S, 29.31, WS_4, 72.08 %. IR data (cm^{-1}): 3067 (υ_{N-H}), 2958, 2875, 1555, 1460, 1378, 1172, 1046, 1011, 989, 850, 748, 463 (υ_3). Raman data (cm^{-1}): 479 (υ_1), 456 (υ_3), 181 (υ_2, υ_4).

Synthesis of bis(*n*-propylammonium) tetrasulfidomolybdate (2)

The reaction of freshly prepared $(NH_4)_2[MoS_4]$ instead of $(NH_4)_2[WS_4]$ with *n*-propylamine under identical conditions as mentioned for (**1**) resulted in the formation of compound (**2**). Alternatively, (**2**) was also prepared starting from MoO_3. Molybdic acid (2 g) was dissolved in a mixture of water (15 mL) and *n*-propylamine (4 mL) in a conical flask. Into this clear solution, a continuous and rapid stream of H_2S gas was passed for ~30 minutes by maintaining the reaction mixture at ~60°C. When red solid started appearing, the gas flow was stopped, the flask stoppered and the reaction mixture was allowed to cool in an ice-bath for ~1 h, resulting in the separation of copious amounts of (**2**). The product was filtered, washed with isopropyl alcohol (10 mL), ether (10 mL) and dried under vacuum. The crystals obtained in this method were used for structure determination (Yield 2.8 g).

Anal.: Calc. for $(C_6H_{20}N_2S_4Mo$ (**2**): C, 20.92; H, 5.85; N, 8.13; S, 37.24; MoS_4, 65.09; Found: C, 20.63; H, 5.83; N, 8.17; S, 37.02, MoS_4, 65.21 %. IR data (cm^{-1}): 3065 (υ_{N-H}), 2956, 2873, 1555, 1460, 1378, 1172, 1046, 1011, 989, 850, 748, 478 (υ_3). Raman data (cm^{-1}): 487 (υ_3), 469, 454 (υ_1), 184 (υ_2, υ_4)
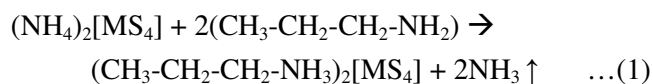
X-ray crystallography

Intensity data for both compounds (**1**) and (**2**) were collected on an Image Plate Diffraction System (IPDS 1) from STOE using graphite-monochromated Mo-Kα radiation. For compound (**1**), a numerical absorption correction was performed. Both the structures were solved with direct methods using SHELXS-97[22] and refinement was done against F^2 using SHELXL-97[22]. All non-hydrogen atoms were refined using anisotropic displacement parameters. The C-H hydrogen atoms were positioned with idealized geometry and were refined using a riding model. The N-H hydrogen atoms were located in difference map, their bond lengths were set to ideal values and afterwards they were refined using a riding model. In both compounds, both *n*-propylammonium cations are located on crystallographic mirror planes and two methylene carbon atoms are disordered due to symmetry. Furthermore, in one of the two cations (N11), the two methylene carbon atoms are disordered. Thus, in this cation, the two methylene carbon atoms are disordered over three positions. The technical details of data acquisition and some selected crystal refinement results for compounds (**1**) and (**2**) are summarized in Table 1.

Results and Discussion
Synthesis and spectral studies

The reaction of an aqueous solution of $(NH_4)_2[MS_4]$ with *n*-propylamine followed by crystallization, resulted in the formation of (**1**) or (**2**). The reactivity characteristics of the tetrahedral $[MS_4]^{2-}$ anion has been investigated with several organic reagents other than amines and it has been shown that $[MS_4]^{2-}$ can function as S-transfer reagents resulting in the formation of novel organo-sulfur compounds[8]. The reaction of organic amines with $[MS_4]^{2-}$, designated by us as a base promoted cation exchange reaction in a very early report[14], differs from the reactions of $[MS_4]^{2-}$ with other organic substrates in that no S-transfer takes place. In the base promoted cation exchange reaction, the stronger organic amine (pK_a of *n*-propylamine = 10.71) displaces the weaker ammonia (pK_a = 9.24) resulting in the exchange of ammonium cations in $(NH_4)_2[MS_4]$ by the organic cation for charge balance (Eq. 1).

$(NH_4)_2[MS_4] + 2(CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_2) \rightarrow$
$\qquad (CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_3)_2[MS_4] + 2NH_3 \uparrow \qquad \ldots(1)$

On reaction with the amine, the tetrahedral $[MS_4]^{2-}$ core retains its identity resulting in the formation of organic tetrasulfidometalates. The reaction of

Table 1—Crystal data and structure refinement for compounds (**1**) and (**2**)

Empirical formula	(C$_6$H$_{20}$N$_2$)[WS$_4$] (**1**)	(C$_6$H$_{20}$N$_2$)[MoS$_4$] (**2**)
Formula weight (g mol^{-1})	432.33	344.42
Temp. (K)	170(2)	170(2)
Wavelength (A)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	P*nma*	P*nma*
a (Å)	9.9714(8)	9.9294(9)
b (Å)	7.0763(5)	7.0306(5)
c (Å)	20.7384(16)	20.7299(13)
α = β = γ (°)	90	90
Vol. (Å^3)	1463.31(19)	1447.15(19)
Z	4	4
D_{calc} (mg/m^3)	1.962	1.581
Absorption coefficient (mm^{-1})	8.433	1.451
F(000)	832	704
Crystal size (mm^3)	0.2 × 0.12 × 0.06	0.12 × 0.1 × 0.1
Θ range for data collection (°)	2.83 to 27.98	2.27 to 28.05
Index ranges	-13 ≤ *h* ≤ 13, -9 ≤ *k* ≤ 9, -19 ≤ *l* ≤ 27	-13 ≤ *h* ≤ 13, -8 ≤ *k* ≤ 9, -27 ≤ *l* ≤ 22
Reflections collected	7762	11117
Independent reflections (R$_{int}$)	1852 (0.0586)	1866 (0.0313)
Completeness to theta	97.0 %	98.3 %
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1852 / 0 / 101	1866 / 0 / 101
Goodness-of-fit on F^2	1.049	1.042
Final *R* indices [I>2σ (I)]	R1 = 0.0331, wR2 = 0.0807	R1 = 0.0354, wR2 = 0.0947
R indices (all data)	R1 = 0.0479, wR2 = 0.0871	R1 = 0.0417, wR2 = 0.0990
Extinction coefficient	0.0031(5)	0.0156(19)
Largest difference peak and hole (e.Å^{-3})	1.221 and -1.906	0.673 and -0.560

(NH$_4$)$_2$[MS$_4$] with *n*-propylamine to form the new compounds (**1**) and (**2**) is in accordance with the known stability of [MS$_4$]$^{2-}$ in alkaline medium[10,11]. Compound (**2**) was also prepared by passing a rapid stream of H$_2$S gas into a solution of molybdic acid dissolved in a mixture of water and *n*-propylamine. It is well documented that the reaction of an ammoniacal molybdate solution with H$_2$S results in the formation of (NH$_4$)$_2$[MoS$_4$][21]. 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$_2$S leading to the formation of an organic [MoS$_4$]$^{2-}$ compound. Both (**1**) and (**2**) which are crystallized from a strongly alkaline medium are not stable in acids and decompose to insoluble metal sulfides on acidification with dilute HCl. On reacting with an aqueous solution of [Ni(en)$_3$]Cl$_2$ both compounds are converted quantitatively into the insoluble [Ni(en)$_3$][MS$_4$][16,23] as shown in Eq. 2. In addition, the title compounds analyzed satisfactorily for the proposed formula. Both compounds are

soluble in water, aqueous ammonia, DMF and DMSO but are insoluble in organic solvents such as CH$_3$CN or CHCl$_3$.

(NH$_4$)$_2$[MS$_4$] + [Ni(en)$_3$]Cl$_2$ →
$\qquad$ 2(NH$_4$)Cl + [Ni(en)$_3$][MS$_4$] ↓ $\quad$ …(2)
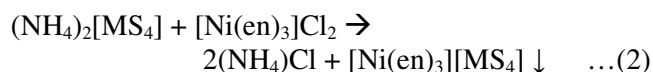
The electronic spectra of (**1**) and (**2**) exhibit characteristic signals which can be assigned for the transition of the [MS$_4$]$^{2-}$ chromophore[16-18]. The infrared spectra of (**1**) and (**2**) are nearly identical and several signals are observed in the mid-infrared spectra above 500 cm^{-1}, which may be attributed to the vibrations of the organic cation. The intense signal at around 3065 cm^{-1} in (**1**) and (**2**) may be assigned for υ$_{N-H}$. The low energy signals below 500 cm^{-1} are due to the vibrations of the [MS$_4$]$^{2-}$ moiety. For both compounds no intense signals are observed below 400 cm^{-1} in their far infrared spectra. For the free tetrahedral [MS$_4$]$^{2-}$ anion, four characteristic vibrations, υ$_1$(A$_1$), υ$_2$(E), υ$_3$(F$_2$) and υ$_4$(F$_2$) are expected, all of which are Raman active while only υ$_3$ and υ$_4$ are IR active. The intense signal at 463 cm^{-1}

in (**1**) is assigned to the triply degenerate $\upsilon_3(F_2)$ asymmetric stretching M-S vibration[21]. The Raman spectrum of (**1**) exhibits an intense signal at 479 cm^{-1}, which can be assigned for the symmetric stretching M-S vibration $\upsilon_1(A_1)$ while the intense signal at 181 cm^{-1} is assigned for the doubly degenerate $\upsilon_2(E)$ and $\upsilon_4(F_2)$ vibrations[21]. The vibrational spectral data of the Mo analogue (**2**) can be similarly explained. The vibrational spectra indicate that the $[MS_4]^{2-}$ tetrahedron in (**1**) and (**2**) is relatively less distorted[23-27].

Crystal structures of (1) and (2)

The X-ray powder pattern of compounds (**1**) and (**2**) are identical indicating their isostructural nature. The isostructural bis(*n*-propylammonium) $[MS_4]^{2-}$ compounds (**1**) and (**2**) crystallize in the centrosymmetric orthorhombic space group P*nma* with both the cations and anions located in special positions. The crystal structures of (**1**) or (**2**) consist of a tetrahedral $[MS_4]^{2-}$ dianion of *m* symmetry [M = W (**1**); M = Mo (**2**)] and two crystallo-graphically independent *n*-propylammonium cations, both of which are situated on mirror planes (Fig. 1). In compound (**1**), the $[WS_4]^{2-}$ tetrahedron is slightly distorted and the S–W–S bond angles range between 108.45(8) and 110.38(5)° (Table 2). The W–S bond lengths vary from 2.1869(9) to 2.195(2) Å with a mean value of 2.1901 Å. In the isostructural $[MoS_4]^{2-}$ compound, the S–Mo–S angles (108.42(4) to 110.49(4)°) indicate a slight distortion of the tetrahedron. The Mo-S bonds range from 2.1833(7) to 2.1876(11) Å with a mean value of 2.1852 Å (Table 2).
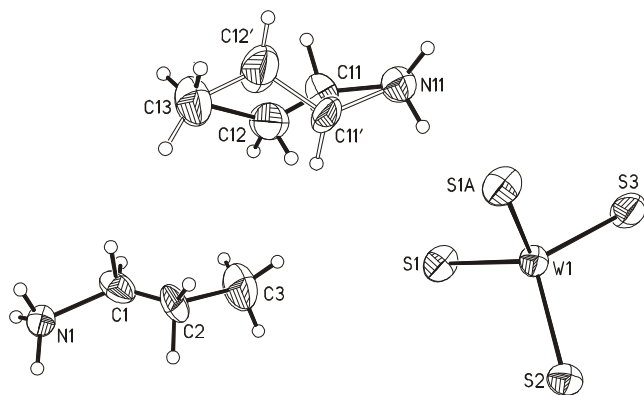

Fig. 1—The crystal structure of $(C_6H_{20}N_2)[WS_4]$ (**1**) showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. The *n*-propylammonium cations are disordered. Symmetry code: A) *x*,-*y*+1/2, *z*. (Note: Compounds (**1**) and (**2**) are isotypic. Hence, only the structure of (**1**) is shown as a representative).

Comparative study of tetrasulfidometalates crystallizing in space group P*nma*

The $[MS_4]^{2-}$ anion is located on a special position *m* and therefore two of the S atoms (S1 and S1A) are located on either side of the mirror plane. This same structural feature of the anion and cations lying on mirror planes, is observed in the group of alkali metal (K$^+$, Rb$^+$ and Cs$^+$), ammonium and methylammonium $[MS_4]^{2-}$ compounds[28-34]. All these compounds crystallize in the orthorhombic space group P*nma* and exhibit two identical M-S distances (Table 3). The difference, Δ, between the longest and shortest M-S bond lengths is 0.0081 for compound (**1**) and 0.0043 Å for (**2**). The Δ values for the two title compounds are significantly smaller than the limiting value of 0.033 Å reported by us for several $[MS_4]^{2-}$ containing compounds[23-27]. Interestingly, these Δ values are the lowest for the group of compounds listed in Table 3 which crystallize in the space group P*nma*. Based on an analysis of Δ values of several $[WS_4]^{2-}$ and $[MoS_4]^{2-}$ compounds we have shown that for compounds with a $\Delta > 0.033$ Å the distortion of the $[MS_4]^{2-}$ tetrahedron leads to the appearance of the υ_1 vibration as well as additional signals in the IR spectrum[23-27]. Thus, the infrared spectra of (**1**) and (**2**) are in accordance with the smaller Δ values.

In both (**1**) and (**2**), two of the M-S bonds are longer than the average M-S bond length while the identical M-S bonds are shorter. Such a distribution of two long and two short M-S distances can be

Table 2—Selected bond lengths (Å) and bond angles (°) for compounds (**1**) and (**2**)

Bond lengths		Bond angles	
(C$_6$H$_{20}$N$_2$)[WS$_4$] (**1**)			
W(1)-S(1)	2.1869(9)	S(1)-W(1)-S(1A)	108.45(8)
W(1)-S(1A)	2.1869(9)	S(1)-W(1)-S(2)	110.38(5)
W(1)-S(2)	2.1916(19)	S(1A)-W(1)-S(2)	110.38(5)
W(1)-S(3)	2.195(2)	S(1)-W(1)-S(3)	108.78(6)
		S(1A)-W(1)-S(3)	108.78(6)
		S(2)-W(1)-S(3)	110.03(8)
(C$_6$H$_{20}$N$_2$)[MoS$_4$] (**2**)			
Mo(1)-S(1)	2.1833(7)	S(1A)-Mo(1)-S(1)	108.42(4)
Mo(1)-S(1A)	2.1833(7)	S(1A)-Mo(1)-S(3)	108.54(3)
Mo(1)-S(3)	2.1867(13)	S(1)-Mo(1)-S(3)	108.54(3)
Mo(1)-S(2)	2.1876(11)	S(1A)-Mo(1)-S(2)	110.39(3)
		S(1)-Mo(1)-S(2)	110.39(3)
		S(3)-Mo(1)-S(2)	110.49(4)

Symmetry transformation used to generate equivalent atoms: A) x,-y+1/2, z.

Table 3—Comparative structural parameters of tetrasulfidometalates crystallising in P*nma* space group

Comp.	M-S (long) (Å)	M-S (short) (Å)	Δ (Å)	Secondary interactions	Ref.
$(CH_3NH_3)_2[WS_4]$	2.2010	2.1862	0.0148	N-H⋯S, C-H⋯S	35
$(CH_3NH_3)_2[MoS_4]$	2.1961	2.1762	0.0199	N-H⋯S, C-H⋯S	36
$(K)_2[WS_4]$	2.1901	2.1758	0.0143	K⋯S	37
$(K)_2[MoS_4]$	2.2000	2.1757	0.0243	K⋯S	28
$Rb_2[WS_4]$	2.2053	2.1710	0.0343	Rb⋯S	29
$Rb_2[MoS_4]$	2.1917	2.1782	0.0135	Rb⋯S	30
$Cs_2[WS_4]$	2.2079	2.1915	0.0164	Cs⋯S	31
$Cs_2[MoS_4]$	2.1935	2.1809	0.0126	Cs⋯S	32
$(NH_4)_2[WS_4]$	2.2090	2.1856	0.0234	N-H⋯S	33
$(NH_4)_2[MoS_4]$	2.186	2.171	0.015	N-H⋯S	34
$(C_6H_{20}N_2)[WS_4]$ (1)	2.195	2.1869	0.0081	N-H⋯S	This work
$(C_6H_{20}N_2)[MoS_4]$ (2)	2.1833	2.1876	0.0043	N-H⋯S	This work

attributed to the weak secondary interactions (N-H⋯S and C-H⋯S) between the organic cations and $[MS_4]^{2-}$ anions. The H atoms attached to N1 and N11 in both compounds exhibit short H⋯S contacts. However, in view of the observed disorder in the cations a detailed correlation of the strength and number of H-bonding interactions with those of the M-S bonds is not presented herein.

In summary, the two organic tetrasulfidometalates described in the present paper constitute two new exampless of organic $[MS_4]^{2-}$ compounds to the growing list of a series of structurally characterized group VI metal chalcogenides.

Supplementary Data

Crystallographic data (excluding structure factors) for the structures reported herein have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 724075 (**1**) and CCDC 724076 (**2**). Copies of these data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (fax: +44-(0)1223-336033 or Email: deposit@ccdc.cam.ac.uk).

Acknowledgement

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