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## Synthesis and structural characterization of two new non-centrosymmetric tetrasulfidometalates

Bikshandarkoil R. Srinivasan<sup>1</sup>, Sunder N. Dhuri<sup>1</sup>, Ashish R. Naik<sup>1</sup>, Christian Näther<sup>2</sup>, and Wolfgang Bensch<sup>2</sup>

<sup>1</sup>Department of Chemistry, Goa University PO  
Goa 403 206 India email; srini@unigoa.ac.in

<sup>2</sup>Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel,  
Max-Eyth Straße 2, D-24118 Kiel, Germany

### Abstract

The synthesis and structural characterization of two new group VI tetrasulfidometalates  $(\text{NH}_4)_6[\text{MS}_4]_3 \cdot (\text{hmt})_4$  (hmt = hexamethylenetetramine; M = W (1); M = Mo (2)) is reported. 1 and 2 are isostructural and crystallize in the non-centrosymmetric trigonal space group R3c. The  $(\text{NH}_4)^+$  cations,  $[\text{MS}_4]^{2-}$  anions and hmt molecules are joined by hydrogen bonding to form a three-dimensional network. In the crystal structure six  $\text{NH}_4^+$  ions and six  $[\text{MS}_4]^{2-}$  anions are arranged to form channels running along [001] hosting a part of the hmt molecules. The channels are surrounded by the remaining hmt molecules. The presence of hmt in the structures of 1 or 2 results in a reduction of the decomposition temperature compared to that of  $(\text{NH}_4)_2[\text{MS}_4]$  and formation of carbon contaminated metal sulfide residues.

Keywords: tetrasulfidometalate; hexamethylenetetramine; trigonal; non-centrosymmetric

## Introduction

The study of soluble group VI tetrasulfidometalate compounds  $[MS_4]^{2-}$  (M = Mo, W) known since the nineteenth century [1] continues to attract the attention of several investigators in a variety of research areas namely catalysis, nano materials, solid state  $^{33}S$  MAS NMR spectroscopy, bioinorganic chemistry and sulfur transfer reagents in organic synthesis etc [2,3]. Several papers reporting on the use of ammonium tetrasulfidomolybdate in therapy for the treatment of diseases have appeared [3]. The ammonium salts of  $[MoS_4]^{2-}$  or  $[WS_4]^{2-}$  routinely used as a starting material for the synthesis of a variety of structurally diverse Mo-S and W-S compounds, can function as pure inorganic ligands forming S-bridged heterometallic compounds [4,5]. A few years ago we initiated a systematic study of the reactions of the group VI tetrasulfidometalates with organic amines [6] as the investigations of tetraalkylammonium halides with  $[MS_4]^{2-}$  leading to the formation of the organic soluble  $[R_4N]_2[MS_4]$  (R=alkyl) were the only known reaction of this type prior to our work [7]. The reaction of amines with  $[MS_4]^{2-}$  differs from the reactions with other organic substrates in that no sulfur transfer takes place. Instead there is only a displacement of the ammonium cation, with the organic amines functioning as cations for charge balance. Using this so called base promoted cation exchange reaction we and others have synthesized and structurally characterized several new organic ammonium tetrathiometalates and have demonstrated that organic ammonium  $[MS_4]^{2-}$  compounds are useful precursors for the formation of carbon contaminated amorphous metal sulfides [8,9].

In our research we have employed several amines, all of which are more basic than ammonia and these reactions always resulted in the formation of tetrasulfidometalate compounds charge balanced by organic cations. In order to extend this chemistry to weaker bases, we have investigated the reaction of  $(NH_3)_2[MS_4]$  with a weak base like

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3 hexamethylenetetramine (hmt). It is interesting to note that the reaction with hmt results in  
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5 the formation of a new hmt adduct  $(\text{NH}_4)_6[\text{MS}_4]_3 \cdot (\text{hmt})_4$  ( $M = \text{W}$  1;  $M = \text{Mo}$  2) and not the  
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7 desired  $(\text{hmtH})_2[\text{MS}_4]$  compounds containing the protonated  $(\text{hmtH})^+$  cation for charge  
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9 balance as has been previously reported [10]. The synthesis, properties and structural  
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11 features of the hexamine adducts are described in this paper.  
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## 14 15 16 Results and Discussion

### 17 18 Description of crystal structures of 1 and 2

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20 Compounds 1 and 2 are isostructural and crystallize in the non-centrosymmetric trigonal  
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22 space group  $R\bar{3}c$ . The crystal structure consists of a tetrahedral  $[\text{MS}_4]^{2-}$  dianion ( $M = \text{W}$  1;  
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24  $M = \text{Mo}$  2), two crystallographically independent ammonium cations which are located in  
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26 general positions and two neutral hmt molecules one of which is situated in a general  
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28 position, whereas the second is located on a 3-fold rotation axis (Figure 1, Supporting  
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30 information Figure S1). The bond distances and bond angles observed for the hmt  
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32 molecules are in the normal range. In compound 1 the  $[\text{WS}_4]^{2-}$  tetrahedron is slightly  
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34 distorted and the S–W–S bond angles range between  $108.65(5)$  and  $110.34(5)^\circ$  (Table 1).  
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36 The W–S distances vary from  $2.1804(12)$  to  $2.2135(12)$  Å with a mean W–S bond length  
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38 of  $2.1938$  Å. The difference  $\Delta$  between the longest and shortest W-S bond is  $0.0331$  Å. In  
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40 the isostructural  $[\text{MoS}_4]^{2-}$  compound the Mo-S distances vary from  $2.1754(9)$  to  $2.2122(9)$   
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42 Å (mean Mo–S bond length:  $2.1908$  Å) and a  $\Delta$  value of  $0.0368$  Å. Two of the observed  
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44 W-S distances (W-S2 and W-S4) are shorter than the mean W-S distance while the other  
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46 two are longer at  $2.1960(11)$  and  $2.2135(12)$  Å respectively indicating a distorted WS  
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48 tetrahedron. In compound 2 a similar distribution of two long and two short Mo-S  
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50 distances is observed.  
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3 The distinct M-S bond distances can be attributed to the several weak hydrogen bonding  
4 interactions observed among the  $[\text{MS}_4]^{2-}$  anions,  $[\text{NH}_4]^+$  cations and hmt molecules. A  
5 scrutiny of the structure of 1 reveals a total of 19 weak hydrogen bonds comprising of  
6 seven N-H $\cdots$ S, four N-H $\cdots$ N and eight C-H $\cdots$ S H-bonding interactions ([Supporting](#)  
7 [information Table S1](#)). Each  $[\text{WS}_4]^{2-}$  ion is linked to five hexamethylenetetramine  
8 molecules with the aid of eight weak C-H $\cdots$ S bonds and to four  $[\text{NH}_4]^+$  cations with the  
9 aid of seven weak N-H $\cdots$ S bonds ([Supporting information Figure S2](#)). The weak N-H $\cdots$ N  
10 interactions link the cations with the neutral hmt into an extended H-bonded chain  
11 resulting in the formation of a cavity ([Figure 2](#)). The  $[\text{WS}_4]^{2-}$  anions are organized into  
12 hexagonal arrays inside this cavity. The neutral hmt solvent molecules line the outer edges  
13 of the hexagon with the aid of weak C-H $\cdots$ S interactions ([Figure 3](#), [Supporting](#)  
14 [information Figure S3-S5](#)). The ammonium cations line the inner edge of the hexagonal  
15  $[\text{WS}_4]^{2-}$  array via N-H $\cdots$ S interactions and on the outer edge the ammonium cations are  
16 linked to the hmt molecules via N-H $\cdots$ N interactions. The net result of the hydrogen  
17 bonding interactions is the organization of six  $\text{NH}_4^+$  ions and six  $[\text{MS}_4]^{2-}$  anions to form  
18 channels running along [001] hosting a part of the hmt molecules. The channels are  
19 surrounded by the remaining hmt molecules. The isostructural compound 2 exhibits an  
20 identical H-bonding behaviour ([Table S1](#)) resulting in the formation of a similar hexagonal  
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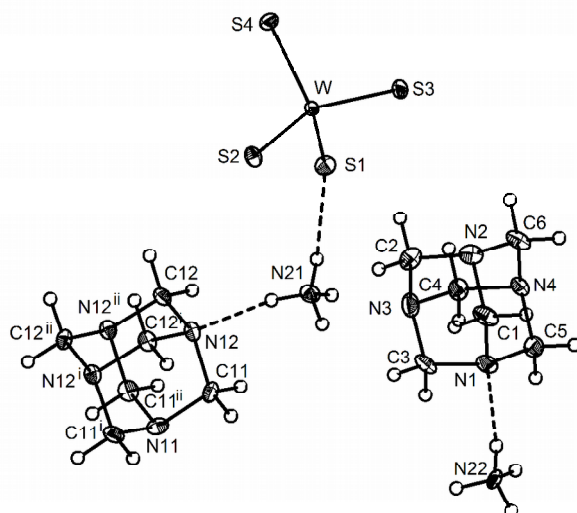


Figure 1. The crystal structure of  $(\text{NH}_4)_6[\text{WS}_4]_3 \cdot (\text{hmt})_4$  (1) showing the atom-labeling scheme. (For the isostructural Mo compound 2 see [Supporting information Figure S1](#)) Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as circles of arbitrary radius. Intramolecular H-bonding is shown as dashed lines. Symmetry code: i)  $-y, x-y, z$  ii)  $-x+y, -x, z$

Table 1. Selected bond lengths and bond angle ( $\text{\AA}$ ,  $^\circ$ ) for 1 and 2

$(\text{NH}_4)_6[\text{WS}_4]_3 \cdot (\text{hmt})_4$ (1)		$(\text{NH}_4)_6[\text{MoS}_4]_3 \cdot (\text{hmt})_4$ (2)	
W-S(2)	2.1804(12)	Mo-S(2)	2.1754(9)
W-S(4)	2.1850(13)	Mo-S(4)	2.1828(9)
W-S(3)	2.1960(11)	Mo-S(3)	2.1923(9)
W-S(1)	2.2135(12)	Mo-S(1)	2.2122(9)
S(2)-W-S(4)	110.34(5)	S(2)-Mo-S(4)	110.42(4)
S(2)-W-S(3)	108.65(5)	S(2)-Mo-S(3)	108.46(3)
S(4)-W-S(3)	108.96(5)	S(4)-Mo-S(3)	108.99(4)
S(2)-W-S(1)	109.49(5)	S(2)-Mo-S(1)	109.48(4)
S(4)-W-S(1)	109.19(5)	S(4)-Mo-S(1)	109.23(4)
S(3)-W-S(1)	110.20(5)	S(3)-Mo-S(1)	110.25(4)

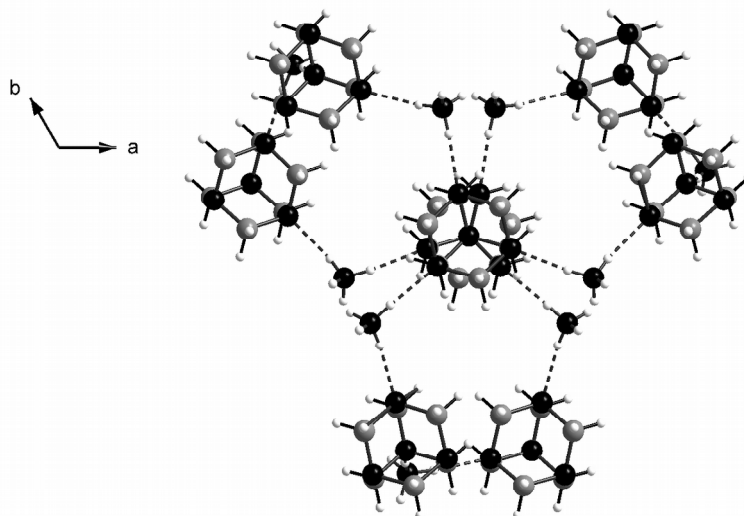


Figure 2 Weak N-H...N interactions link the cations with hmt into an extended H-bonded chain resulting in the formation of a cavity.

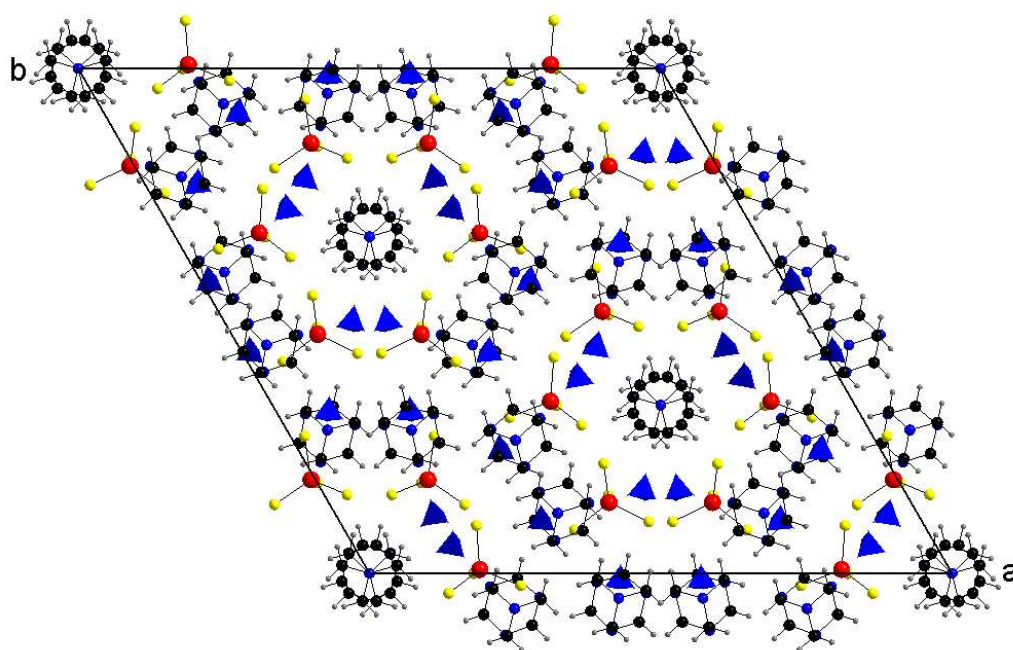
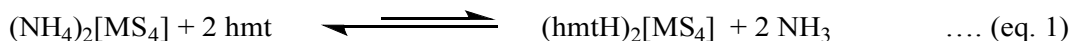


Figure 3. Crystal structure of  $(\text{NH}_4)_6[\text{WS}_4]_3 \cdot (\text{hmt})_4$  (1) with view along the c axis. The ammonium cations are represented as polyhedra. For clarity, H-bonds are not shown.

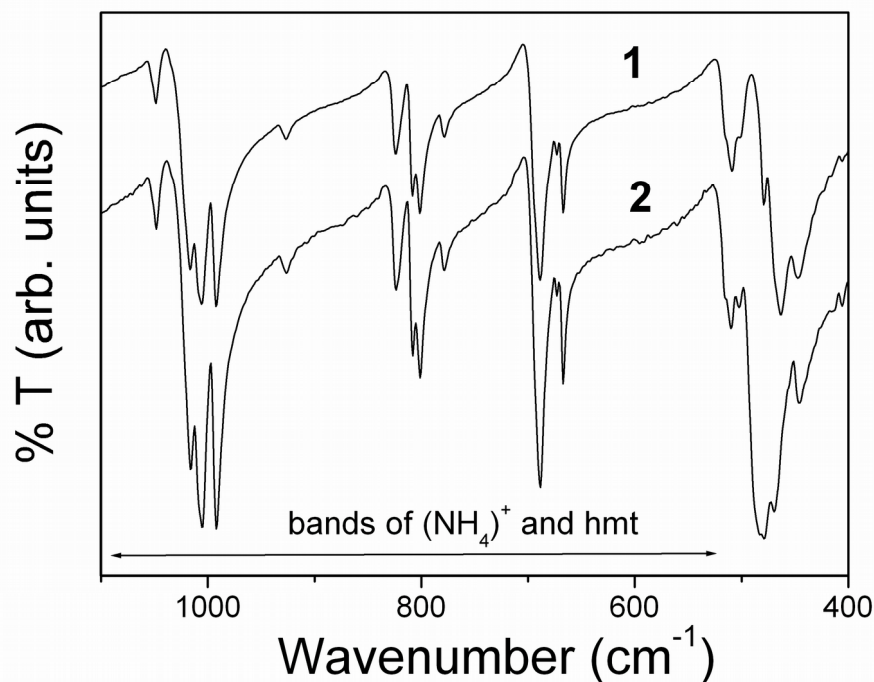
Synthesis, spectroscopy and thermal investigations

Heating of an aqueous solution of  $(\text{NH}_4)_2[\text{MS}_4]$  with hexamine in a 1:2 molar ratio followed by recrystallization afforded the hmt adducts 1 or 2 in good yield. In a previous paper an aqueous reaction of  $\text{MoO}_3$  with excess hmt followed by treatment with  $\text{H}_2\text{S}$  gas was reported to result in the formation of water soluble red  $(\text{hmtH})_2[\text{MoS}_4]$  solid which was characterized by IR and UV-Vis spectra [10]. A reinvestigation of this reaction reveals that no water soluble product can be isolated. In view of the difficulties in the reproducible nature of this reported method for  $(\text{hmtH})_2[\text{MoS}_4]$ , the reaction of a hot aqueous solution of  $(\text{NH}_4)_2[\text{MS}_4]$  with hexamine was investigated. In earlier work we have demonstrated that a more basic organic amine reacts with  $(\text{NH}_4)_2[\text{MS}_4]$  displacing the weaker ammonia [6, 8]. The pH of a 0.1 M solution of hmt is  $\sim 8$  and its pka is 4.89 as compared to that of ammonia (pka = 9.24). Hence the equilibrium of the reaction of  $(\text{NH}_4)_2[\text{MS}_4]$  with hmt (equation 1) is not expected to favor the formation of a product with a  $(\text{hmtH})^+$  cation.



The heating of the reaction mixture was done in order to achieve a metathesis reaction, as the volatile ammonia can be removed on heating, to favor formation of  $(\text{hmtH})_2[\text{MS}_4]$ . However, even under this condition, no product containing protonated hmt could be obtained. Instead, the product of this reaction analysed for a new hmt adduct compound containing  $(\text{NH}_4)^+$ ,  $(\text{MS}_4)^{2-}$  and hmt in the ratio of 6:3:4. The incorporation of hmt in 1 or 2 was evidenced based on their characteristic NMR spectra which exhibit a single signal for the equivalent  $-\text{CH}_2$  protons. The electronic spectra of 1 and 2 in water exhibit signals which can be assigned to the intra ligand charge transitions of  $[\text{MS}_4]^{2-}$  chromophore and the observed values are in good agreement with reported data [4].

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3 The infrared spectra of the isotopic compounds 1 and 2 are nearly identical concerning the  
4 shapes and number of signals. The signals observed above  $500\text{ cm}^{-1}$  are caused by  
5 vibrations of the ammonium cation and the neutral hexamine, while the bands below  $500$   
6  $\text{cm}^{-1}$  are due to the vibrations of the  $[\text{MS}_4]^{2-}$  moiety (Figure 4). The signal at  $509\text{ cm}^{-1}$  can  
7 be assigned to an internal vibration of the tricyclic hmt moiety as a strong band is  
8 observed at  $514\text{ cm}^{-1}$  in free hmt. This low energy signal has no contribution from the  
9  $\{\text{MS}_4\}$  tetrahedron as it is observed at the same energy in both compounds. The triply  
10 degenerate asymmetric stretching M-S vibration appears as a split band ( $469, 447\text{ cm}^{-1}$  for  
11 1 and  $473$  and  $447\text{ cm}^{-1}$  for 2) in both compounds indicating distortion of the tetrahedron  
12 in terms of the difference  $\Delta$  between the longest and shortest M-S distances [8].  
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49 Figure 4. Infrared spectra of compounds 1 (top) and 2 (bottom) showing the split M-S  
50 vibration below  $500\text{ cm}^{-1}$ .  
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54 In order to understand the thermal behavior of the title compounds, the TG-DTA curves of  
55  $(\text{NH}_4)_2[\text{MS}_4]$  were also recorded in addition to those of 1 and 2. The title compounds  
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3 exhibit only endothermic thermal processes unlike  $(\text{NH}_4)_2[\text{MS}_4]$  which shows an  
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5 endothermic step for decomposition of  $\text{NH}_4^+$  and an exothermic step for the formation of  
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7 metal disulfide [11]. Compared to  $(\text{NH}_4)_2[\text{WS}_4]$ , the decomposition of 1 containing hmt  
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9 solvate molecules begins at a relatively lower temperature with a DTA peak at 178 °C with  
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11 another closely related endothermic process at 208 °C (Supporting information Figure S6).  
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13 For the isostructural compound 2, a first endothermic event is observed at 181 °C. Under  
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15 identical experimental conditions, the thermal decomposition pattern of 2 is very similar to  
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17 that of 1 (Supporting information Figure S7).  
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21 The thermal behavior of 1 and 2 is very similar to that of organic  $[\text{MS}]$  compounds  
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23 which decompose endothermically. It is well documented that such compounds exhibit a  
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25 complex thermal behavior involving structural phase transitions as well as emissions of  
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27 different organic fragments [12]. In view of the absence of associated mass spectral data of  
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29 the emitted fragments, no assignment of the exact nature of the decomposition process is  
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31 made for 1 and 2. The residual mass (57.0% for 1 and 42.1% for 2) for the final residues  
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33 is more than the expected value (46.3% for 1 and 35.8% for 2) for the formation of  
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35 stoichiometric  $\text{MS}_2$ . This observation can be explained due to the presence of considerable  
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37 amounts of carbon (13.8% for 1 and 10.7% for 2) determined from the elemental analysis  
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39 of the residues.  
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## 42 43 Conclusions

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45 In this work, we have described the synthesis and structural characterization of hmt  
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47 adducts of ammonium tetrasulfidometals in phase pure form. The compounds which  
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49 crystallize in non-centrosymmetric space group exhibit three varieties of H-bonding  
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51 interactions among the anion, ammonium cation and hmt. The title compounds decompose  
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53 at lower temperatures as compared to ammonium tetrasulfidometalates, resulting in the  
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55 formation of carbon contaminated metal sulfide residues.  
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## Experimental

### Materials and methods

All the chemicals used in this study were of reagent grade and were used as received.

$(\text{NH}_4)_2[\text{MS}_4]$  ( $\text{M} = \text{Mo}, \text{W}$ ) were prepared by a published procedure [13]. IR spectra were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer in the range  $4000\text{-}400\text{ cm}^{-1}$ .

The samples for the IR spectra were diluted with KBr in the solid state and the signals referenced to polystyrene bands. UV-visible spectra were recorded on a Shimadzu UV-2450 double beam spectrophotometer using matched quartz cells. TG-DTA measurements were performed in flowing air, in  $\text{Al}_2\text{O}_3$  crucibles on a STA-409 simultaneous thermal analyzer from Netzsch. A heating rate of  $4\text{ K min}^{-1}$  was employed for all measurements.

#### 2.2 Preparation of $(\text{NH}_4)_6[\text{MS}_4]_3 \cdot (\text{hmt})_4$ ( $\text{M}=\text{W}$ 1; $\text{M}=\text{Mo}$ 2)

$(\text{NH}_4)_2[\text{WS}_4]$  (1.740 g, 5 mmol) was dissolved in water (20 ml) containing hmt (1.40 g, 10 mmol). A few drops of ammonia were added into the reaction mixture. The clear yellow solution was heated on a water bath for  $\sim 5$  min. The hot reaction mixture was filtered and the clear filtrate left aside for crystallization. The yellow blocks of crystals which separated after about 2 weeks were isolated by filtration, washed with 2-propanol (15 ml) followed by diethyl ether and air dried to yield 1.2 g of compound 1. The use of freshly prepared  $(\text{NH}_4)_2[\text{MoS}_4]$  (1.30 g, 5 mmol) instead of  $(\text{NH}_4)_2[\text{WS}_4]$  in the above reaction afforded compound 2 in 53% yield. The crystals thus obtained are suitable for X-ray structure determination.

Analytical data: Calc. for  $\text{C}_{24}\text{H}_{72}\text{N}_{22}\text{W}_3\text{S}_{12}$  (1): C 17.96; H, 4.52; N, 19.20; S, 23.97;  $\text{WS}_4$  58.33; Found: C, 18.00; H, 4.52, N, 18.92; S, 24.71;  $\text{WS}_4$ , 58.25 %.

IR data: 3182, 2949, 2878, 2641, 2210, 1904, 1682, 1462, 1389, 1339, 1236, 1011, 993, 928, 824, 802, 692, 668, 509, 469, 447,  $374\text{ cm}^{-1}$ .

$^1\text{H NMR}$  ( $\text{D}_2\text{O}$ )  $\delta$  (in ppm) : 2.9 (s)

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3 UV-Vis (in water): 394 (17100), 278 (25290), 216 (30875) nm

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5 Analytical data: Calc. for  $C_{24}H_{72}N_{22}Mo_3S_{12}$  (2): C, 21.49; H, 5.41; N, 22.97; S, 28.68;  
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7  $MoS_4$  50.13; Found: C, 21.50; H, 5.39, N, 22.38; S, 29.51;  $MoS_4$ , 50.09 %.

8  
9 IR data: 3167, 2947, 2878, 2675, 2210, 1896, 1692, 1456, 1386, 1338, 1234, 1009, 993,  
10  
11 928, 824, 802, 692, 668, 509, 473, 447, 374  $cm^{-1}$ .

12  
13  
14  $^1H$  NMR ( $D_2O$ )  $\delta$  (in ppm): (2.9 s)

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16 UV-Vis (in water): 469 (12310), 318 (16600), 242 (23618) nm

#### 17 18 19 20 21 X-ray crystal structure determination

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23 Intensity data for compounds 1 and 2 were collected on a STOE Image Plate Diffraction  
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25 System (IPDS-1) using graphite-monochromated Mo-K $\alpha$  radiation. The raw intensities  
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27 were corrected for absorption using X-red and X-Shape. The structure was solved with  
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29 direct methods using SHELXS-97 [14] and refinement was done against F2 using  
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31 SHELXL-97 [14]. All non-hydrogen atoms were refined anisotropically. The C-H H  
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33 atoms were introduced at their calculated positions and refined isotropic with  $U_{iso}(H) = 1.2$   
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35  $U_{eq}(C)$  using a riding model.. The N-H H atoms of the ammonium cations were located in  
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37 the difference Fourier map, their bond lengths were set to ideal values and afterwards they  
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39 were refined with  $U_{iso}(H) = 1.5 U_{eq}(N)$  using a riding model. The absolute structures for 1  
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41 and 2 were determined and according to the Flack x-parameter they are in agreement with  
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43 the selected setting. Technical details of data acquisition and some selected refinement results  
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45 are summarized in Table 2.

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49 Crystallographic data (excluding structure factors) for the structures reported in this paper  
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51 have been deposited with the Cambridge Crystallographic Data Centre as supplementary  
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53 publication no. CCDC-910056 (1) and CCDC-910055 (2). Copies of the data can be  
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3 obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ,  
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5 UK. (Fax: +44-1223-336033, <http://www.ccdc.cam.ac.uk/conts/retrieving.html>; E-Mail:  
6  
7 [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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11 Supporting information (see footnote on the first page of this article):

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13 Additional figures related to crystal structure, IR spectra, thermograms, and Listing of H-  
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15 bonding geometry for 1 and 2. (Figures S1–S7, Table S1).

#### 16 17 18 19 20 Acknowledgements

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Table 2 Crystal data and structure refinement for compounds 1 and 2

	(NH <sub>4</sub> ) <sub>6</sub> [WS <sub>4</sub> ] <sub>3</sub> ·(hmt) <sub>4</sub> (1)	(NH <sub>4</sub> ) <sub>6</sub> [MoS <sub>4</sub> ] <sub>3</sub> ·(hmt) <sub>4</sub> (2)
Empirical formula	C <sub>24</sub> H <sub>72</sub> N <sub>22</sub> W <sub>3</sub> S <sub>12</sub>	C <sub>24</sub> H <sub>72</sub> N <sub>22</sub> Mo <sub>3</sub> S <sub>12</sub>
Formula weight (g mol <sup>-1</sup> )	1605.29	1341.59
Temperature (K)	170(2)	170(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Trigonal	Trigonal
Space group	R3c	R3c
a (Å <sup>o</sup> )	28.2227(17)	28.1819(18)
b (Å <sup>o</sup> )	28.2227(17)	28.1819(18)
c (Å <sup>o</sup> )	11.8847(7)	11.8846(7)
α = β (°)	90	90
γ (°)	120	120
Volume (Å <sup>3</sup> )	8198.1(8)	8174.4(9)
Z	6	6
D <sub>calc</sub> (mg/m <sup>3</sup> )	1.951	1.635
Absorption coefficient (mm <sup>-1</sup> )	6.802	1.184
F(000)	4704	4128
Crystal size (mm <sup>3</sup> )	0.12 x 0.1 x 0.08	0.12 x 0.09 x 0.07
Theta range for data collection (°)	2.79 to 30.41	2.80 to 30.42
Index ranges	-40 ≤ h ≤ 40, -39 ≤ k ≤ 40, -16 ≤ l ≤ 15	-40 ≤ h ≤ 39, -39 ≤ k ≤ 40, -16 ≤ l ≤ 16
Reflections collected	31803	31731
Independent reflections (R <sub>int</sub> )	5328 (0.0354)	5466 (0.0434)
Completeness to theta	99.8 %	99.7 %
Min/max transmission	0.3387 / 0.4234	0.7962 / 0.8731
Refinement method	full-matrix least-squares on F <sup>2</sup>	full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5328 / 1 / 185	5466 / 1 / 185
Goodness-of-fit on F <sup>2</sup>	1.042	1.053
Final R indices [I > 2σ(I)]	R1 = 0.0281, wR2 = 0.0720	R1 = 0.0377, wR2 = 0.0950
R indices (all data)	R1 = 0.0287, wR2 = 0.0724	R1 = 0.0412, wR2 = 0.0972
Flack-x-parameter	0.020 (6)	0.03 (3)
Largest diff. peak and hole (e.Å <sup>-3</sup> )	1.571 and -1.684	0.741 and -1.180

## References:

[1] a) J. J. Berzelius, Poggendorffs Ann. Phys. Lpz. 1826, 7, 262; b) J. J. Berzelius, Poggendorffs Ann. Phys. Lpz. 1826, 8, 269; c) G. Krüss, Justus Liebigs Ann Chem, 1884 225, 1; d) E. Corleis, Justus Liebigs Ann Chem, 1886 232, 244.

[2] a) S. E. Skrabalak, K. S. Suslick, J. Am. Chem. Soc. 2005, 127, 9990; b) S. Bag, A.F. Gaudette, M.E. Bussell, M.G. Kanatzidis, Nature Chem., 2009, 1, 217; c) M. Shafaei-Fallah, C.D. Malliakas, M.G. Kanatzidis, Z. Anorg. Allg. Chem. 2012, 683, 2594; d) H.J. Jakobsen, H. Bildsoe, J. Skibsted, M. Brorson, B.R. Srinivasan, C. Näther, W. Bensch. Phys. Chem. Chem. Phys., 2009, 11, 6981; e) H.J. Jakobsen, H. Bildsoe, J. Skibsted, M.R. Hansen, M. Brorson, B.R. Srinivasan, W. Bensch. Inorg. Chem. 2009, 48, 1787; f) M. Polyakov, M. Poisot, W. Bensch, M. Muhler, W. Grünert, J. Catal. 2008 256, 137; g) M. Polyakov, S. Indris, S. Schwamborn, A. Mazheika, M. Poisot, L. Kienle, W. Bensch, M. Muhler, W. Grünert. J. Catal. 2008, 260, 236; h) M. Polyakov, M.W.E. van den Berg, T. Hanft, M. Poisot, W. Bensch, M. Muhler, W. Grünert. J. Catal. 2008, 256, 126; i) D. Coucouvanis, Acc. Chem. Res. 1981, 14, 201; j) R.H. Holm, Chem. Soc. Rev. 1981, 10, 455; k) E.I. Stiefel, Prog. Inorg. Chem. 1973, 22, 1 ; l) K. R. Prabhu, N. Devan, S. Chandrasekaran, Synlett 2002, 11, 1762.

[3] a) G. J. Brewer, Inorg. Chim. Acta 2012, 393, 135 and references therein; b) G. J. Brewer, R. Dick, C. Zeng, G. Hou, J. Inorg. BioChem. 2006, 100, 927; c) F. Askari, D. Innis, R.B. Dick, G. Hou, J. Marrero, J. Greenson , G.J. Brewer, Trans Res, 2010, 155, 123; d) G.J. Brewer, Seminars in Integrative Medicine, 2003, 1, 181; e) G. Hou, R. Dick, C. Zeng, G.J. Brewer, Translational Research 2006, 309-314; f) H.M. Alvarez, Y. Xue, C.D. Robinson, M.A. Canalizo-Hernández, R.G. Marvin, R.A. Kelly, A. Mondragón, J.E. Penner-Hahn, T. V. O'Halloran, Science 2010, 327, 331.

[4] a) E. Diemann, A. Müller, Coord. Chem. Rev. 1973, 10, 79; b) A. Müller, E. Diemann, R. Jostes, H. Bögge, Angew. Chem. 1981, 93, 957; Angew. Chem. Int. Ed. Engl. 1981, 20, 934 and references cited therein.

[5] a) D. Coucouvanis, Adv. Inorg. Chem. 1998, 45, 1; b) T. Shibahara, Coord. Chem. Rev. 1993, 123, 73; c) T. B. Rauchfuss, Inorg. Chem. 2004, 43, 14; d) D. E. Schwarz, T. B. Rauchfuss, S. R. Wilson, Inorg. Chem. 2003, 42, 2410; e) E.I. Stiefel, T.R. Halbert, C.L. Coyle, L. Wei, W.-H.Pan, T.C. Ho, R.R. Chianeeli, M. Daage, Polyhedron 1989, 8, 1625; f) M.A. Harmer, T.R. Halbert, W.-H.Pan, C.L. Coyle, S.A. Cohen, E.I. Stiefel, Polyhedron 1986, 5, 347.

[6] a) B. R. Srinivasan, B. K. Vernekar, K. Nagarajan, Indian J. Chem. 2001, 40A, 563; b) B. R. Srinivasan, S. N. Dhuri, C. Näther, W. Bensch, Acta Crystallogr. 2002, E58, m622; c) B. R. Srinivasan, S. N. Dhuri, C. Näther, W. Bensch, Acta Crystallogr. 2003, C59, m124.

[7] T.E. Wolff, J.M. Berg, K.O. Hodgson, R.B. Frankel, R.H. Holm, J. Am. Chem. Soc. 1979, 101, 4140; b) A.R. Ramesha, S. Chandrasekaran, Synth. Commun. 1992, 22, 3277; c) G. Alonso, G.Aguirre, I.A. Rivero, S. Fuentes, Inorg. Chim. Acta 1998, 274, 108.

1  
2  
3  
4 [8] a) U. Siemeling, F. Bretthauer, C. Bruhn, *Z. Anorg. Allg. Chem.* 2006, 632, 1027; b)  
5 M. Poisot, C. Näther, W. Bensch, *Z. Naturforsch.* 2007, 62b, 209; c) B. R. Srinivasan, S.  
6 N. Dhuri, C. Näther, W. Bensch, *Monatsh. Chem.* 2006, 137, 397; d) B.R. Srinivasan, C.  
7 Näther, S.N. Dhuri, W. Bensch, *Polyhedron* 2006, 25, 3269; e) B. R. Srinivasan, C.  
8 Näther, W. Bensch, *Acta Crystallogr.* 2006, C62, m98. f) B. R. Srinivasan, A.R. Naik, C.  
9 Näther, W. Bensch, *Z. Anorg. Allg. Chem.* 2007, 633, 582.

10  
11  
12 [9] a) B. R. Srinivasan, S. N. Dhuri, C. Näther, W. Bensch, *Inorg. Chim. Acta* 2005, 358,  
13 279; b) B. R. Srinivasan, S. N. Dhuri, M. Poisot, C. Näther, W. Bensch, *Z. Naturforsch.*  
14 2004, 59b, 1083; c) B. R. Srinivasan, S. N. Dhuri, M. Poisot, C. Näther, W. Bensch, *Z.*  
15 *Anorg. Allg. Chem.* 2005, 631, 1087; d) B. R. Srinivasan, S. N. Dhuri, C. Näther, W.  
16 Bensch, *Transition Met. Chem.* 2007, 32, 64. e) B.R. Srinivasan, S.N. Dhuri, A.R. Naik,  
17 C. Näther, W. Bensch, *Polyhedron*, 2008, 27, 25; f) B.R. Srinivasan, A.R. Naik, M.Poisot,  
18 C. Näther, W. Bensch, *Polyhedron* 2009, 28, 1379-1385 (2009); g) B.R. Srinivasan, A.R.  
19 Naik, S.N. Dhuri, C. Näther, W. Bensch, *Polyhedron*, 2009, 28, 3715;

20  
21  
22 [10] M.R. Udupa, G.Aravamudan, *Current Sci.* 1973, 42 676.

23  
24 [11] T.P. Prasad, E. Diemann, A. Müller, *J. Inorg. Nucl. Chem.* 1973, 35, 1895.

25  
26 [12] a) M. Poisot, W. Bensch, S. Fuentes, G. Alonso, *Thermochim. Acta.* 2006, 444, 35;  
27 b) M. Poisot, W. Bensch, *Thermochim. Acta*, 2007, 453, 42.

28  
29  
30 [13] J. W. McDonald, G. D. Friesen, L. D. Rosenhein, W. E. Newton, *Inorg. Chim. Acta*  
31 1983, 72, 205.

32  
33 [14] G. M. Sheldrick, *Acta Crystallogr., Sect. A* 2008, 64, 112.

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3 Synthesis and structural characterization of two new  
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6 non-centrosymmetric tetrasulfidometalates  
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10 Bikshandarkoil R. Srinivasan <sup>1</sup>, Sunder N. Dhuri <sup>1</sup>, Ashish R. Naik <sup>1</sup>, Christian  
11 Näther <sup>2</sup>, and Wolfgang Bensch <sup>2</sup>  
12

13 <sup>1</sup>Department of Chemistry, Goa University PO  
14 Goa 403 206 India email; srini@unigoa.ac.in

15 <sup>2</sup>Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel,  
16 Max-Eyth Straße 2, D-24118 Kiel, Germany  
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20 Graphical Abstract

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22 The synthesis and structural characterization of two new group VI tetrasulfidometalates  
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24  $(\text{NH}_4)_6[\text{MS}_4]_3 \cdot (\text{hmt})_4$  (hmt = hexamethylenetetramine; M = W (1); M = Mo (2)) is  
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