Synthesis, spectroscopic, thermal and X-ray structure characterization of 1,3-propanediammonium tetrathiomolybdate and N,N,N′,N′-tetramethylethylenediammonium tetrathiomolybdate[†]

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[†] Dedicated to Prof. S.S. Krishnamurthy on the occasion of his 65th birthday

Abstract

The title compounds 1,3-propanediammonium tetrathiomolybdate, (1,3-pnH$_2$)[MoS$_4$], **1** and N,N,N′,N′-tetramethylethylenediammonium tetrathiomolybdate, (tmenH$_2$)[MoS$_4$], **2** were prepared by reacting the ammonium salt of [MoS$_4$]$^{2-}$ with the corresponding organic diamine. In **1** and **2** the organic diamines (1,3-pn is 1,3-propanediamine, and tmen is N,N,N′,N′-tetramethylethylenediamine) are present in their diprotonated form. The reaction of **1** or **2** with [Ni(en)$_3$]Cl$_2$.2H$_2$O (en is ethylenediamine) results in the formation of the highly insoluble complex tris(ethylenediamine)Ni(II) tetrathiomolybdate, [Ni(en)$_3$][MoS$_4$] in quantitative yields. **1** and **2** have been characterized by chemical analysis, vibrational, UV-Vis and NMR spectroscopy, TG-DTA-MS and single crystal X-ray crystallography. Compound **1** is thermally more stable compared to **2**. Both complexes decompose in a single step forming amorphous molybdenum sulfide. The structure of the title complexes can be described as consisting of tetrahedral [MoS$_4$]$^{2-}$ dianions which accept a complex series of H-bonds from the organic dications. The strength and number of these hydrogen bonds affect the Mo-S bond lengths.

Keywords : 1,3-propanediammonium, tetramethylethylenediammonium, tris(ethylenediamine)Ni(II), tetrathiomolybdate, and H-bonds

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Graphical Abstract

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The title compounds 1,3-propanediammonium tetrathiomolybdate **1** and N,N,N′,N′-tetramethylethylenediammonium tetrathiomolybdate, **2** were prepared by reacting the ammonium salt of $[MoS_4]^{2-}$ with the corresponding organic diamine. The two diamines have different steric bulk and different numbers of potential hydrogen-bonding donors. This results in different crystal packings viz. a three-dimensional network in **1** and isolated groups consisting of two cations and two anions in **2**.

1

2
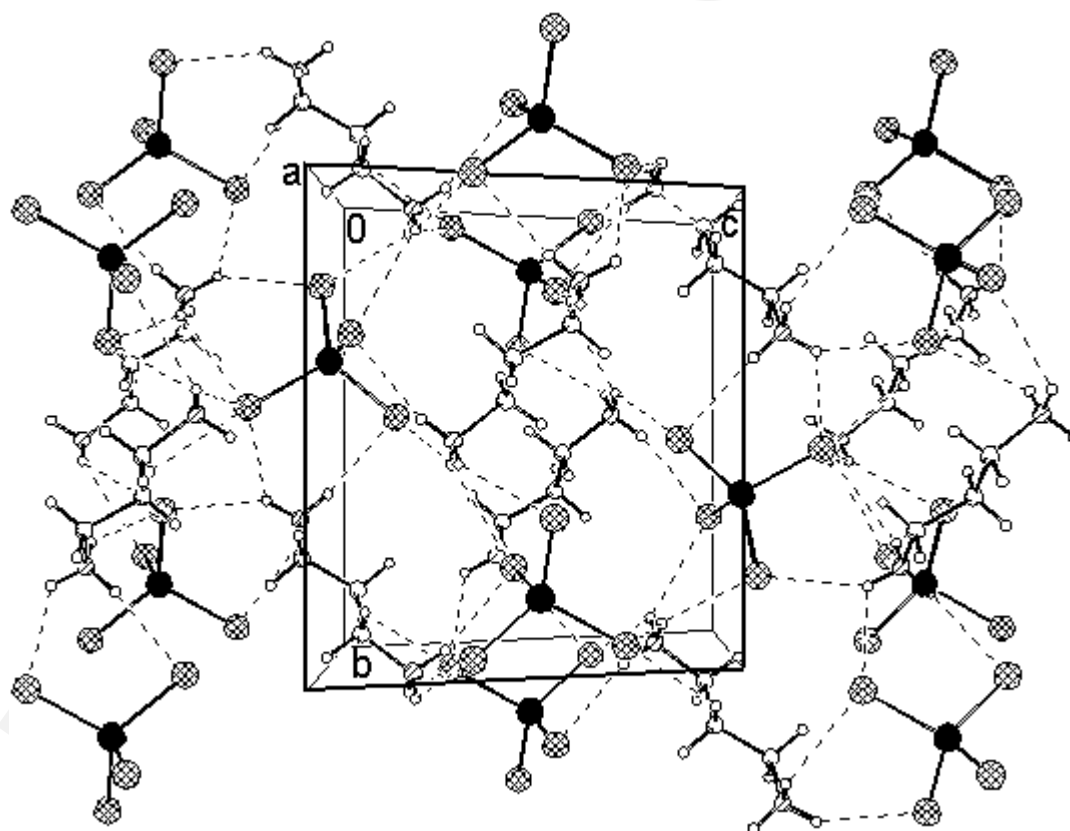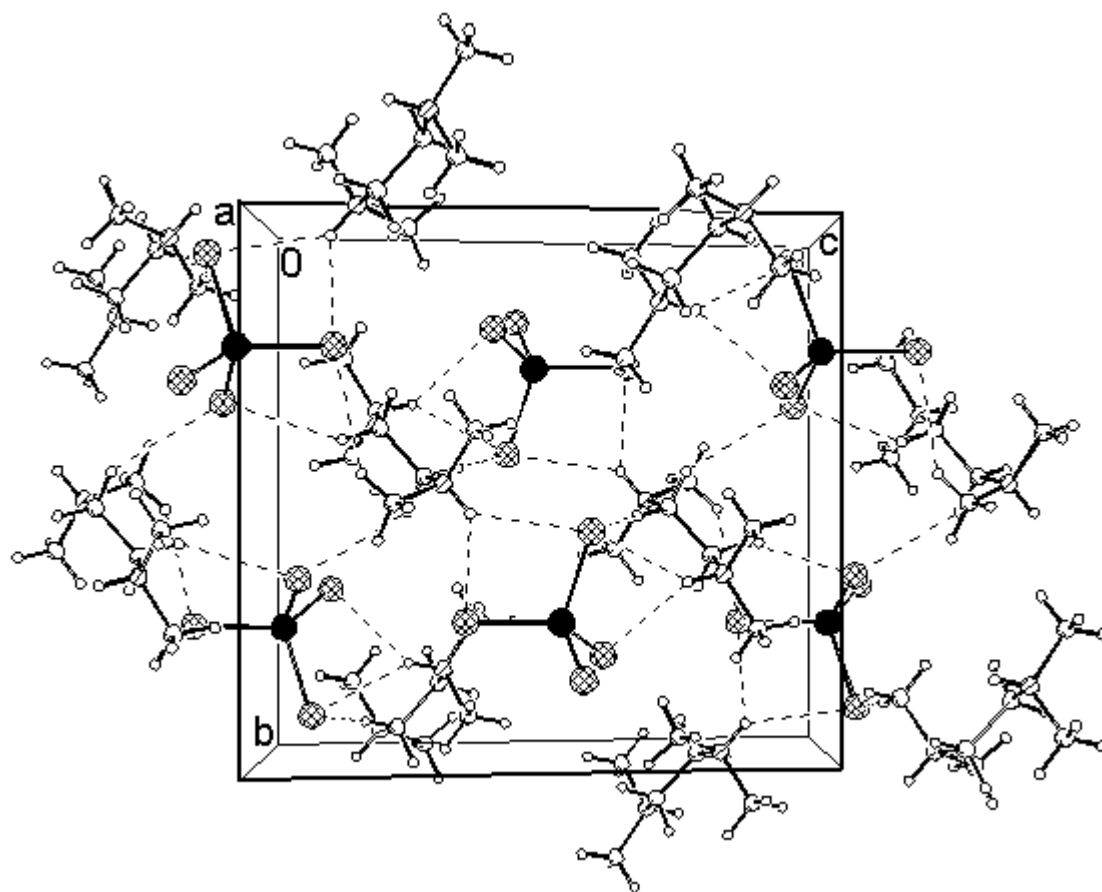
1. Introduction

The sulfur complexes of Mo are a unique class of compounds, encompassing an unusually wide range of metal to sulfur stoichiometries, metal oxidation states, coordination geometries and different bonding modes of the sulfido ligands [1]. The diversity in structural and reactivity characteristics is an important reason for the continuing research in this rapidly growing field. The Mo-S complexes like $[MoS(S_4)_2]^{2-}$, $[Mo_2(S)_2(\mu-S)_2(S_2)_2]^{2-}$, $[Mo_2(S)_2(\mu-S)_2(S_4)(S_2)]^{2-}$, $[Mo_2(S)_2(\mu-S)_2(S_4)_2]^{2-}$, $[SMo(MoS_4)_2]^{2-}$ etc. which can be prepared from $[MoS_4]^{2-}$ by reacting with the appropriate reagents, can serve as few examples to illustrate the structural diversity encountered in Mo-S chemistry [2-6]. It is well documented that the $[MoS_4]^{2-}$ ion can behave like a bidentate ligand to form sulfur bridged multi-metal complexes [7,8]. In addition to the ammonium salt of tetrathiomolybdate $(NH_4)_2[MoS_4]$ **3,** which is routinely used as the starting material in synthetic Mo-S chemistry, other tetrathiomolybdate salts of organic ammonium cations like ethylenediammonium [9] tetraethylammonium [10] and benzyltriethylammonium [11] are also known.

The accessibility of phase pure sulphido complexes of Mo like $[Ni(en)_3][MoS_4]$ (en is ethylenediamine) $[Co_2(tren)_3][MoS_4]_2$ (tren is tris(2-aminoethyl)amine) and the spectacular bicapped molybdenum cluster $[N(CH_3)_4]_4[Mo_6O_6S_{14}]$ from a reaction mixture of tetraoxomolybdate, elemental sulphur, amine and a metal salt under mild solvothermal conditions, has added a new dimension to Mo-S chemistry [12-16]. It has been observed that in solvothermal reactions the product formation is probably influenced by the type of amine (base) used in the synthesis. Thus the use of ammonia resulted in the formation of the well-known trinuclear $[Mo_3S_{13}]^{2-}$ complex [16] while the use of a chelating amine like en yielded the simple $[MoS_4]^{2-}$ containing complexes [12,13]. The use of a mixture of $[(CH_3)_4N]OH$ and ammonia gave the novel hexanuclear $[Mo_6O_6S_{14}]^{2-}$ complex [15]. It has also been reported that benzyltriethylammonium tetrathiomolybdate can be used as a sulfur-transfer reagent in organic synthesis for the formation of novel organo-sulfur compounds under mild reaction conditions [11, 17]. Although the reactions of thiomolybdates with several organic compounds like alkyl halides [17], alcohols etc. have been investigated, relatively little work has been done with respect to the reactions of thiomolybdates with organic amines [9]. Hence it was of interest to

investigate the reactivity of Mo-S complexes with organic amines. In the present study, we have chosen two different diamines namely 1,3-propanediamine (1,3-pn) and N,N,N′,N′-tetramethylethylenediamine (tmen) for the reactions with ammonium tetrathiomolybdate. Both diamines readily afford the corresponding organic diammonium salts of $[MoS_4]^{2-}$ **1** and **2** in good yields. The two diamines used in this study have different steric bulk and different numbers of potential hydrogen bonding donors. This gives rise to different crystal packing viz. a three dimensional network in **1** and isolated groups consisting of two cations and two anions in **2**. The results of these investigations are described in this paper.

2. Experimental

2.1 Materials and Methods

Solvents and reagents were used in this investigation as obtained from commercial sources. $(NH_4)_2[MoS_4]$ [10] and $[Ni(en)_3]Cl_2.2H_2O$ [18] were prepared by literature methods. Far-IR spectra (range 80 to 500 cm^{-1}) were measured on a Bruker IFS 66 Infrared Spectrometer in pressed polyethylene disks. MIR spectra of the compound were recorded in a KBr matrix. The sample was ground with dry KBr into a fine powder and pressed into a transparent pellet. The spectra were recorded in the IR region of 450 to 3000 cm^{-1}, (resolution 1 cm^{-1}) with a ATI Mattson Genesis Infrared-Spectrometer. Raman spectra were measured in the region from 100 to 3500 cm^{-1} on a Bruker IFS 66 Fourier transform Raman spectrometer. UV-Vis spectra were recorded on a Shimadzu UV-1601 instrument using matched quartz cells. ^{1}H NMR spectra were recorded on a Bruker 300 MHz FT-NMR instrument. DTA-TG-MS measurements were performed simultaneously using the STA-409CD device (Netzsch) with Skimmer coupling, which was equipped with a quadrupole mass spectrometer QMA 400 (max. 512 amu) from Balzers. The MS measurements were performed in analogue and trend scan mode. The investigations were performed in Al_2O_3 crucibles under a dynamic helium atmosphere (flow rate 75 mL/min, purity 4.6) using a heating rate of 4°K/min up to 500°C. All measurements were corrected for buoyancy and current effects. The instrument was calibrated using standard reference materials.

2.2 Preparation of (1,3-pnH₂)[MoS₄] 1

Method 1:

Freshly prepared $(NH_4)_2[MoS_4]$ (520 mg, 2 mmol) was dissolved in distilled water (15 ml) and 1,3-pn (0.4 ml) was added at room temperature. The reaction mixture was filtered and the clear filtrate was left undisturbed in the refrigerator. After 2 days well formed, deep red blocks of **1** crystallized out. The crystals were filtered, washed with cold water (~5 ml) followed by isopropanol (~5 ml), ether and air-dried. Yield of the pure product was 550 mg (90%). The crystals obtained in this method were suitable for X-ray studies.

IR data: 3006 (br), 1544, 1451, 1398, 1305, 1202, 1097, 943, 751, 484 (v_3), 475, 207, 175 (v_4), 116, cm^{-1}.

Raman Data: 484, 453 (v_1), 197, 187 and 171 (v_2) cm^{-1}.

UV-Vis data (H_2O): 468 nm ($\varepsilon=8740$), 317 nm ($\varepsilon=14020$), 241 nm ($\varepsilon=21490$).

^1H NMR (DMSO-d_6): δ 1.85 ppm (p, 2H, J=7.5 Hz), δ 2.88 ppm (t, 4H, J=7.5 Hz), δ 7.60 ppm (br, -NH3).

Anal. Found (Calcd): C 12.08 (12.00), H 4.09 (4.04), N 8.98 (9.34), S 42.62 (42.66) Mo 31.32 (31.94) %.

Method 2 :

MoO_3 (1 g) was taken in a mixture of water (30 ml) and 1,3-pn (1 ml). The reaction mixture was filtered and a rapid stream of H_2S gas was passed into the filtrate for 30-40 min. The gas flow was stopped when crystals started to appear. The reaction mixture was left aside for crystallization. The deep red crystals of **1** were filtered, washed with cold water (15 ml) and isopropanol (10 ml) followed by ether and dried under vacuum. The product obtained (1.64 g) in this method had an identical infrared spectrum and analyzed satisfactorily as the product from method 1.

2.3 Preparation of (tmenH₂)[MoS₄] 2

Method 1

The use of tmen (0.5 ml) instead of 1,3-pn in the preparation of the 1,3-propanediammonium salt resulted in the formation of the (tmenH₂) salt of tetrathiomolybdate **2** in 75% yield.

IR data: 2982, 1439, 1405, 1408, 1355, 1319, 1189, 1045, 963, 840, 810, 782, 479 (ν_3), 452, 196 (ν_4), 126, 102 cm^{-1}.

Raman : 484 (ν_3), 468, 453 (ν_1), 183, 173 (ν_2) cm^{-1}.

Method 2

       Compound **2** was also prepared from MoO_3 (1 g) and tmen (2.5 ml) by following the same procedure adopted for **1** in Method 2. The product obtained (1.54 g) had an identical infrared spectrum as that obtained from method 1 and analyzed satisfactorily as the product from Method 1. The crystals obtained in this method were suitable for X-ray studies.

UV-Vis data (H_2O): 476 nm (ε=7030), 324 (ε=10040), 250 nm (ε=15330).

^{1}H NMR (D_2O): δ 3.40 ppm (s, 4H), δ 2.80 ppm (s, 12H).

Anal. Found (Calcd): C 21.05 (21.06), H 5.32 (5.31), N 7.99 (8.19), S 37.31 (37.41) Mo 27.05 (28.03) %.

2.4 Preparation of [Ni(en)₃][MoS₄]

       To a well stirred solution of $[Ni(en)_3]Cl_2.2H_2O$ (350 mg) in water (20 ml) was slowly added in drops an aqueous ammonia solution (20 ml of H_2O and 2 ml of NH_3) containing 1 mmol of **1** or **2**. This resulted in the immediate precipitation of a fine orange-red powder. The reaction mixture was stirred for 1 h and left aside. It was then filtered and the precipitate washed with water, followed by isopropanol and then air dried resulting in the formation of 463 mg of the product. The product analyzed satisfactorily as $[Ni(en)_3][MoS_4]$. Yield was quantitative.

IR data: 3287, 3258, 3236, 3143, 2928, 2876, 1563, 1453, 1325, 1279, 1119, 1028, 967, 851, 652, 516, 471, cm^{-1}.

3. Results and Discussion

3.1 Synthetic aspects

       The synthesis of the title complexes can be readily accomplished in good yields by reacting $(NH_4)_2[MoS_4]$ with the corresponding organic diamine (Method 1) or by the exhaustive hydrogen sulfide treatment of an aqueous molybdic acid solution in the presence of the organic diamine (Method 2). The formation of the title

complexes **1** or **2** from ammonium tetrathiomolybdate on treatment with 1,3-pn or tmen can be explained as a base promoted cation exchange reaction, wherein the stronger organic base replaces the weak ammonia of $(NH_4)_2[MoS_4]$ as shown below. We have used a similar methodology for the isolation of the ethylenediammonium [9,19], and piperazinium [20] salts of $[MS_4]^{2-}$ (M = Mo, W) indicating the generality of this reaction.

$$(NH_4)_2[MoS_4] + \text{1,3-pn or tmen} \quad \rightarrow \textbf{1} \ \text{or}\ \textbf{2} + 2\,NH_3 \tag{1}$$
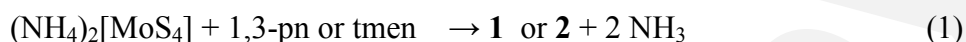
In method 2, the title complexes are prepared by a modification of the method used for the preparation of ammonium tetrathiomolybdate [10]**.** Thus **1** and **2** are obtained in good yields by reacting an aqueous solution of MoO_3 in the presence of the corresponding organic diamine (instead of ammonia for $(NH_4)_2[MoS_4]$) with H_2S. The formation of the $[MoS_4]^{2-}$ complexes under these reaction conditions indicates the stability of the $[MoS_4]^{2-}$ core in an alkaline medium. In contrast, the acidification of the reaction mixtures results in the formation of insoluble MoS_3.

Both complexes **1** and **2** are quite stable in air and less soluble in water compared to the ammonium salt. **1** and **2** are soluble in aqueous ammonia, DMF, DMSO but insoluble in common organic solvents like CH_2Cl_2 $CHCl_3$, CH_3CN etc. Freshly prepared $(NH_4)_2[MoS_4]$ is dark red but the surface color darkens within a day, accompanied by changes in its IR spectrum when left in the open laboratory atmosphere. This aging process has been studied by IR spectroscopy and the surface change has been attributed to the slow decomposition of $(NH_4)_2[MoS_4]$ in air, via an induced electron transfer reaction, resulting in the formation of the dinuclear $[Mo_2O_2S_6]^{2-}$ complex [21]. In contrast, **1** and **2** are quite stable and retain their IR spectral characteristics. This stability can be attributed to the counter ions, which are the dications $(\text{1,3-pnH}_2)^{2+}$ and $(\text{tmenH}_2)^{2+}$. The high stability of the title compounds can be further attributed to the hydrogen bonding interactions of the tetrathiomolybadate anion with the organic cation via N-H···S bonds (vide infra) as established by X-ray analysis.

The reaction of an ammoniacal solution of **1** or **2** with an aqueous solution of [Ni(en)$_3$]Cl$_2$.2H$_2$O resulted in the formation of the previously reported [Ni(en)$_3$][MoS$_4$] complex [12] in quantitative yields. In an earlier report, Müller et al had shown that the reaction of aqueous Ni(II) with [MS$_4$]$^{2-}$ (M = Mo, W) in a 1:2 molar ratio, in the presence of an organic cation like (PPh$_4$)$^{+}$ resulted in the formation of the bis-tetrathiometallato complex of Ni(II) namely (PPh$_4$)$_2$[Ni(MS$_4$)$_2$], wherein the thiometallate acts as a bidentate ligand [22, 23]. In the present study, the use of a coordinatively saturated Ni complex like [Ni(en)$_3$]$^{2+}$ results in the formation of the [Ni(en)$_3$][MoS$_4$] complex where [MoS$_4$]$^{2-}$ functions as an anion. This observation indicates that [MoS$_4$]$^{2-}$ is a weaker ligand as compared to en for Ni(II). [Ni(en)$_3$][MoS$_4$] is highly insoluble and unlike **1** or **2** does not dissolve in ammonia or excess en. However, all the three complexes are unstable in acidic media and decompose to form insoluble sulfides, which exhibit featureless infrared spectra. Thus these complexes can also find use as precursors for the preparation of metal sulfide materials of wide applications. In addition, the tetrathiomolybdate salts of ammonium, ethylenediammonium, piperazinium etc. also react with [Ni(en)$_3$]Cl$_2$.2H$_2$O under ammoniacal conditions to give [Ni(en)$_3$][MoS$_4$]. The high insoluble nature as well as its quantitative formation thus constitutes a method for the estimation of Mo content of organic diammonium tetrathiomolybdates in ammoniacal medium. Interestingly [Ni(en)$_3$][MoS$_4$] has also been obtained by us earlier in very high yields under solvothermal conditions [12]. The high insoluble nature of [Ni(en)$_3$][MoS$_4$] seems to be the driving force for the formation of this product even under solvothermal conditions.

3.2 Spectral studies

A combination of IR, Raman, UV-Vis and ^{1}H NMR techniques has been employed to characterize compounds **1** and **2**. Several bands in the middle of the IR can be attributed to absorptions of the the organic cations. For the [MS$_4$]$^{2-}$ anion four characteristic bands ν_1(A$_1$), ν_2(E), ν_3(F$_2$), and ν_4(F$_2$) are expected in the IR spectra [24]. All four bands are Raman active while only ν_3 and ν_4 are infrared active. The strong signals at 484, 479 cm^{-1} for **1, 2** respectively in the IR spectra can be assigned to the triply degenerate asymmetric stretching vibration (ν_3) of the Mo=S bond [7,24],

while the bands at 207 and 196 cm^{-1} can be assigned to the ν_4 mode. The intense signals in the Raman spectra at 453 cm^{-1} for both complexes is due to the symmetric stretching ν_1 vibration while the strong band around 170 cm^{-1} is assignable to ν_2. These assignments are in good agreement with the literature values [7,24]. The N-H stretching vibrations appear at around 3000 cm^{-1} in **1** and **2** and the shift to lower wave numbers compared to the free amines is due to the H bonding interactions (N-H$\cdots$S). The electronic spectra of the title complexes in H$_2$O exhibit bands at around 460, 320 and 240 nm. The peak positions observed in **1** and **2** are almost identical within experimental error to the corresponding ammonium or tetraethylammonium salts [10] and can be assigned to charge transfer transitions of the tetrahedral [MoS$_4$]$^{2-}$ moiety.

The ^{1}H NMR spectrum of **1** in DMSO-d_6 exhibits three signals at $\delta = 1.85$ (J=7.5 Hz), $\delta = 2.88$ (J=7.5Hz) and $\delta = 7.60$ ppm, respectively. The observed chemical shifts and the coupling constants are as expected for aliphatic amines. The five line signal at $\delta = 1.85$ ppm can be assigned to the absorption of the protons on the central carbon, while the triplet located at $\delta = 2.88$ ppm originates from the resonance of the equivalent protons on the terminal carbons. The broad resonance at $\delta = 7.60$ ppm is due to the absorption of the ammonium protons. The signal of the –NH$_3$ protons in the ethylenediammonium salts of [MS$_4$]$^{2-}$ (M = Mo, W) is also observed as a broad signal at around 7.80 ppm in DMSO-d_6 [25]. The NMR spectrum of **2** exhibits two singlets at $\delta = 3.40$ and $\delta = 2.80$ ppm respectively in D$_2$O. Based on the reported spectrum of tetramethylethylenediammonium dichromate [26], which absorbs at $\delta = 3.8$ ppm (s, 4H) and $\delta = 3.11$ ppm (s, 12H) in D$_2$O as well as the integration of the signals, the resonance at $\delta = 3.40$ ppm can be assigned to the equivalent methylene protons. The signal at $\delta = 2.80$ ppm can be attributed to the methyl protons. The up-field shifting of the resonances in **2** as compared to the dichromate complex can be explained based on the differing nature of the anions. Thus the NMR spectral data conclusively prove the presence of the organic moieties in **1** and **2**.

3.3 Single crystal X-ray diffractometry

Intensity data were collected on a STOE Imaging Plate Diffraction System (IPDS I) for **1** and a Philips PW 1100 four-circle diffractometer for **2** using graphite monochromated Mo-K$_\alpha$ radiation. Lattice parameters were obtained by the least squares refinement of 8000 reflections for **1** and 82 reflections for **2**. The raw intensities were treated in the usual way applying a Lorentz, polarisation correction. The structure was solved with direct methods using SHELXS-94 [27] and refinement was done against F^2 using SHELXL-97 [28]. For compound **1** a numerical absorption correction was applied. Anisotropic displacement parameters were used for C, N, S, and Mo while the H atoms were positioned in idealized geometry and refined using the riding model with fixed isotropic displacement parameters. The technical details of data acquisition and some selected refinement results are summarized in Table 1. The atomic coordinates and equivalent isotropic displacement parameters for **1** and **2** are presented in Table 2. Selected bond lengths and bond angles for **1** and **2** are listed in Tables 3 and 5 respectively.

3.4 Description of the crystal structures of 1 and 2

Both complexes contain the tetrahedral [MoS$_4$]$^{2-}$ dianions and the counter cations are 1,3-propanediammonium in **1**, and tetramethylethylenediammonium in **2**. The structures of the anions in **1** and **2** are presented in Figs. 1 and 3. Complex **1** is isostructural with the corresponding W analog (1,3-pnH$_2$)[WS$_4$] reported by us recently [29]. The substitution of W by Mo in **1** has resulted in a slight decrease in the unit cell volume (unit cell volume of the W complex is 1073.5 (4) Å^3). This can be explained based on the smaller size of Mo. In **1** the (1,3-pnH$_2$)$^{2+}$ dications and [MoS$_4$]$^{2-}$ anions are connected via weak H bonds. The MoS$_4$ tetrahedron in **1** is slightly distorted with S-Mo-S angles between 108.16(3) and 110.43(3)º. The Mo-S bond lengths range from 2.1699(8) to 2.1882(7) Å with an average of 2.1815 Å. (Table 3). All structural parameters of the anion in **1** are in good agreement with those reported for other compounds containing [MoS$_4$]$^{2-}$ such as (enH$_2$)[MoS$_4$] [9] [Ni(en)$_3$][MoS$_4$] [12]. However, three of the Mo-S bond distances in **1** are slightly longer than the average Mo-S bond length of 2.177(6) Å reported for the bis(tetraethylammonium) tetrathiomolybdate complex [(Et$_4$)N]$_2$[MoS$_4$] by Kanatzidis

and Coucouvanis [30]. In $[(Et_4N)]_2[MoS_4]$ the N atoms are tetra-alkylated and it has been reported that there are no intermolecular interactions between the anions and cations. This is expected, as the tetra-alkylated N atom has no H atom for H···S bonds. In the $(1,3\text{-pnH}_2)^{2+}$ dication each N atom is bound to three H atoms and one carbon. In compound **1** seven short intermolecular contacts between the S atoms of $[MoS_4]^{2-}$ and the H atoms of the $(1,3\text{-pnH}_2)^{2+}$ ranging from 2.494 to 2.827 Å are observed (Table 4). The longest Mo-S distance of 2.1882 Å is observed for S1, which makes three contacts while the shortest Mo-S bond length is found for S3 which has a single short S···H contact of 2.683 Å. Although S2 makes a single short contact the Mo-S2 bond length is longer compared to Mo-S4 indicating that H bonding interactions are stronger in this case as seen by the larger N-H···S bond angle of 162.97°. The N-H···S angles ranging from 128.74 to 162.97° indicate different degrees of S···H bond strengths (Fig. 2). Thus, the lengthening of Mo-S bond distances can be attributed to the strength of the H bonding interactions.

The compound **2** differs from **1** in that the organic cation is the tetramethylethylenediammonium dication. Compound **2** is isostructural with the corresponding W analog $(tmenH_2)[WS_4]$ reported by us recently [29], and again the substitution of W by Mo leads to a smaller unit cell volume (1391.5 (2) $Å^3$ for the W complex) due to the smaller size of Mo(VI). In **2**, tetrahedral $[MoS_4]^{2-}$ dianions and tetramethylethylenediammonium dications are observed (Fig. 3). The S-Mo-S bond angles scatter in a very narrow range from 109.08(3) to 109.72(3)° pointing to very little distortion from ideal tetrahedral geometry. The Mo-S bond distances are between 2.1694(8) and 2.1983(8) Å, with a mean Mo-S bond length of 2.1838 Å (Table 5). These structural parameters are in good agreement with those reported for the $[Co_2(tren)_3][MoS_4]_2$ complex [14] which exhibits short S···H contacts between the cation and anion ranging from 2.542 to 2.846 Å. The Mo-S2 bond distance of 2.1983(8) Å in **2** is considerably longer than the average Mo-S bond length of 2.177(6) Å in $[(Et_4N)]_2[MoS_4]$ [30] and the longest Mo-S distance of 2.1882(7) Å found in compound **1**. The N atom in the organic cation in compound **2** carries a single H atom and three alkyl groups unlike in **1** where each N atom is bound to three H atoms and one C atom. In view of the fewer number of H atoms in **2**, only four short intermolecular contacts are observed (Table 6). The S2 atom is involved in two

short contacts while the S1 and S3 atoms each only have one relatively short contact. It is to be noted that there is no S4···H contact. The N-H···S bond angles range from 129.62 and 143.82° (Fig. 4) with the larger values found for S2···H (Table 6). It is well documented that short S···H distances that are accompanied by large N-H···S angles yield the strongest H bonds. Therefore, the interpretation of the differing Mo-S bond lengths is straightforward. The shortest Mo-S bond is found for the S4 atom (2.1694(8) Å) which has no hydrogen bond. Furthermore, S2 has two contacts with N-H···S2 angles around 140° that weaken the Mo-S interaction yielding the longest Mo-S bond of 2.1983(8) Å. Intermediate Mo-S distances are observed to S1 and S3 with one S···H contact each and N-H···S angles significantly smaller than 140°. Because **1** and **2** contain different numbers of hydrogen bonds, different crystal packings are generated with a three-dimensional network in **1** and isolated groups consisting of two cations and two anions in **2** (compare Figs. 2 and 4).

4. Thermoanalytical investigations

Both compounds were studied by TG-DTA coupled with mass spectrometry with the aim to understand the nature of the decomposition processes as well as the products. The results of these investigations are presented in Figs. 5 and 6. The thermal decomposition of $(NH_4)_2[MoS_4]$, which starts at 155^oC is well documented [7, 31] and has been represented by the following process.

$$(NH_4)_2[MoS_4] \rightarrow 2\ NH_3 + H_2S + MoS_3 \qquad (2)$$
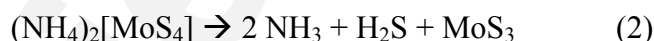
The intermediate formed trisulfide has been reported to be stable till about 335^oC followed by decomposition to elemental sulfur and MoS_2. The title complexes **1** and **2** containing the organic diammonium cations decompose to give amorphous molybdenum sulfide (MoS_3) as the final product with simultaneous emission of the organic amine as well as H_2S (see below). The amorphous nature of the residue is evident from the X-ray powder pattern, which exhibits broad humps but no sharp signals. If compound **1** is heated in the thermobalance a strong endothermic signal is observed at a peak temperature of about 190°C, which is accompanied with a mass loss in the TG curve (Fig. 5). From the DTG curve it is obvious that this event consists of two different steps and the MS curves show that only 1,3-pn (m/z = 57) and H_2S (m/z = 34) is emitted. On further heating the sample mass drops smoothly

which is accompanied with the emission of only H_2S (m/z = 34). The total experimental mass loss up to 600°C of 38.2 % is slightly higher than that expected for the emission of 1,3-pn and H_2S (Δm_{theo}: 36.0%). However, additional measurements using analog scans gave no hints for the emission of elemental sulfur. But the mass change starting from about 350°C is very smooth and therefore, it is difficult to detect small amounts of sulfur emitted by the sample. If compound **2** is investigated a similar behavior as for compound **1** is found. In contrast to **1** decomposition starts at about 112°C and tmen (m/z = 58) is emitted over a larger temperature range (Fig. 6). The total mass loss of 43.0% is slightly lower than that expected for the emission of only tmen and H_2S (Δm_{theo}: 43.9%). A comparison of the TG-DTA curves of the compounds indicates that **2** which contains the bulky tetramethylethylenediammonium cation starts decomposing at a relatively lower temperature of 112°C (endothermic peak) as compared to **1** whose decomposition temperature is much higher with T_{peak} at 190°C. This observation indicates that in **1** the 1,3-propanediammonium cation is more strongly bound compared to the tetramethylethylenediammonium cation in **2**. This can be explained with the structural data where seven short N-H⋯S contacts are observed between the cation and anion in **1** and only four such contacts in **2**. The average N⋯S distance in **1** is also shorter (3.35 Å) than in **2** (3.43 Å). Furthermore **1** has the shortest S⋯H separation (2.494 Å) and the average S⋯H distance is also significantly shorter (2.607 Å) than in **2** (2.710 Å). These observations indicate that the stability of thiomolybdates can be tuned by choosing amines, which have different numbers of potential H bonding donors. Efforts to synthesize such different thiomolybdate compound with other amines are under way.

5. Conclusions

The title compounds **1** and **2** can be readily synthesized in good yields by reacting the ammonium salt of tetrathiomolybdate with the corresponding organic diamine under ambient conditions. The formation of the complexes by the base promoted cation exchange reaction or by the exhaustive hydrogen sulfide treatment indicates that the tetrahedral $[MoS_4]^{2-}$ core is stable under alkaline conditions and remains intact. Furthermore, compounds **1** and **2** react with $[Ni(en)_3]Cl_2.2H_2O$ resulting in the formation of the previously reported $[Ni(en)_3][MoS_4]$ complex [12]

in quantitative yields. The X-ray structural investigation of **1** and **2** indicates that organic diamines are involved in H bonding interactions through the H atoms of the N atoms with the S atoms of the $[MoS_4]^{2-}$ dianion. The differing Mo-S bond distances are explained on the basis of the strengths of the S···H contacts. Because **1** and **2** contain a different number of H bonds, a different packing of anions and cations are generated viz. a three-dimensional network in **1** and isolated groups consisting of two cations and two anions in **2**. The different thermal stability of **1** and **2** can be explained based on the strength and number of S···H interactions between the organic ammonium cations and the tetrathiomolybdate anions.

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 197079 (**1**) and CCDC 197080 (**2**). Copies of the 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).

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Table 1

Technical details of data acquisition and selected refinement results

for $(1,3\text{-pnH}_2)[\text{MoS}_4]$ **1** and $(\text{tmenH}_2)[\text{MoS}_4]$ **2**

Compound	$(1,3\text{-pnH}_2)[\text{MoS}_4]$ **1**	$(\text{tmenH}_2)[\text{MoS}_4]$ **2**
Formula	$C_3H_{12}MoN_2S_4$	$C_6H_{18}MoN_2S_4$
Temperature [K]	293	293
Wavelength [pm]	71.073	71.073
Space group	$P2_1/c$	$P2_1/n$
a [Å]	10.7690 (8)	8.5739 (7)
b [Å]	10.5732 (6)	12.3370 (10)
c [Å]	10.7041 (8)	13.3336 (10)
β [°]	119.569 (1)	101.082 (6)
Volume [$Å^3$]	1060.2 (1)	1384.08 (19)
Z	4	4
μ [mm^{-1}]	1.97	1.52
F(000)	600	696
Molecular weight [g/mol]	300.33	342.40
Density (calcd.) [$g\ cm^{-3}$]	1.882	1.643
Crystal size (in mm)	0.15 0.1 ·0.06	0.16 0.1 0.07
2θ range	3° - 56°	3° - 54°
Reflections collected	10233	4336
Reflections unique	2536	3019
Data (Fo>4σ(Fo)	2366	2202
$R_{int.}$	0.0317	0.0219
Min./Max transmission	0.6550 / 0.7933	
Δρ [e/$Å^3$]	-0.78 /0.70	-0.34 / 0.37
Parameters	92	118
R1 [Fo>4σ(Fo)][a]	0.0307	0.0242
WR2 for all unique data	0.0837	0.0558
Goodness of fit	1.051	0.989

[a]$R1 = \Sigma \left| \left| Fo \right| - \left| Fc \right| \right| / \Sigma \left| F o \right|$

Table 2

Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for **1** and **2.**

Atom	x		y		z		U_{eq}	
(1,3-pnH$_2$)[MoS$_4$] **1**								
Mo(1)	2430	(1)	1451	(1)	4849	(1)	22	(1)
S(1)	1160	(1)	3155	(1)	4550	(1)	29	(1)
S(2)	2351	(1)	239	(1)	6462	(1)	33	(1)
S(3)	1511	(1)	451	(1)	2816	(1)	34	(1)
S(4)	4629	(1)	1988	(1)	5526	(1)	43	(1)
N(1)	5906	(3)	5281	(3)	3032	(3)	37	(1)
C(1)	6352	(3)	4428	(3)	4285	(4)	36	(1)
C(2)	7545	(4)	3563	(3)	4470	(4)	35	(1)
C(3)	8173	(3)	2849	(3)	5865	(3)	35	(1)
N(2)	9365	(3)	2037	(2)	6043	(3)	31	(1)
(tmenH$_2$)[MoS$_4$] **2**								
Mo(1)	7283	(1)	7402	(1)	5232	(1)	25	(1)
S(1)	6430	(1)	7408	(1)	3577	(1)	35	(1)
S(2)	7789	(1)	5725	(1)	5751	(1)	39	(1)
S(3)	5451	(1)	8082	(1)	5976	(1)	39	(1)
S(4)	9430	(1)	8368	(1)	5608	(1)	41	(1)
C(1)	7882	(3)	3878	(2)	3769	(2)	41	(1)
C(2)	7975	(4)	5197	(2)	2389	(2)	43	(1)
N(1)	7114	(2)	4848	(2)	3205	(2)	28	(1)
C(3)	5364	(3)	4708	(2)	2830	(2)	29	(1)
C(4)	4998	(3)	3802	(2)	2058	(2)	33	(1)
N(2)	3293	(2)	3466	(2)	1919	(2)	28	(1)
C(5)	3019	(4)	2445	(3)	1321	(3)	48	(1)
C(6)	2174	(4)	4327	(3)	1449	(3)	54	(1)

U_{eq} are calculated as a third of the trace of the orthogonalised U_{ij} tensors

Table 3
Selected geometric parameters (Å, °) for (1,3-pnH$_2$)[MoS$_4$] **1**

Mo(1)-S(3)	2.1699 (8)	N(1)-C(1)	1.486 (4)
Mo(1)-S(4)	2.1821 (8)	C(1)-C(2)	1.509 (4)
Mo(1)-S(2)	2.1859 (7)	C(2)-C(3)	1.504 (4)
Mo(1)-S(1)	2.1882 (7)	C(3)-N(2)	1.476 (4)
S(3)- Mo(1) -S(4)	110.08 (4)	S(3)- Mo(1) -S(2)	109.27 (3)
S(4)- Mo(1) -S(2)	110.43 (3)	S(3)- Mo(1) -S(1)	108.16 (3)
S(4)- Mo(1) -S(1)	109.40 (3)	S(2)- Mo(1) -S(1)	109.47 (3)
N(1)- C(1) -C(2)	111.2 (3)	C(3)- C(2) -C(1)	111.8 (3)
N(2)- C(3) –C(2)	110.9 (3)		

Table 4
Hydrogen-bonding geometry (Å, °) for (1,3-pnH$_2$)[MoS$_4$] **1**

D-H…A	d(D-H)	d(H…A)	d(D…A)	<DHA	Symmetry code
N1-H1...S4	0.890	2.827	3.454	128.74	–x+1, -y+1, -z+1
N1-H2...S4	0.890	2.494	3.347	160.72	x, -y+1/2, z-1/2;
N1-H3...S3	0.890	2.683	3.330	130.42	–x+1, y+1/2, -z+1/2
N1-H3...S1	0.890	2.685	3.369	134.52	–x+1, -y+1, -z+1
N2-H1...S1	0.890	2.509	3.273	144.20	x+1, -y+1/2, z+1/2
N2-H2...S1	0.890	2.520	3.277	143.30	x+1, y, z
N2-H3...S2	0.890	2.531	3.392	162.97	–x+1, -y, -z+1

D = Donor; A = Acceptor

Table 5
Selected geometric parameters (Å, °) for (tmenH$_2$)[MoS$_4$] **2**

Mo(1)-S(4)	2.1694 (8)	C(1)-N(1)	1.498 (3)
Mo(1)-S(3)	2.1805 (7)	C(2)-N(1)	1.491 (3)
Mo(1)-S(1)	2.1870 (7)	N(1)-C(3)	1.497 (3)
Mo(1)-S(2)	2.1983 (8)	C(3)-C(4)	1.511 (4)
C(4)-N(2)	1.497 (3)	N(2)-C(5)	1.485 (3)
N(2)-C(6)	1.488 (3)		
S(4)- Mo(1) -S(3)	109.69 (3)	S(4)- Mo(1) -S(1)	109.59 (3)
S(3)- Mo(1) -S(1)	109.08 (3)	S(4)- Mo(1) -S(2)	109.72 (3)
S(3)- Mo(1) -S(2)	109.57 (3)	S(1)- Mo(1) -S(2)	109.18 (3)
C(2)- N(1) -C(3)	113.3 (2)	C(2)- N(1) –C(1)	111.4 (2)
C(3)- N(1) –C(1)	113.0 (2)	N(1)-C(3)-C(4)	112.1 (2)
N(2)-C(4)-C(3)	111.1 (2)	C(5)-N(2)-C(6)	110.9 (2)
C(5)-N(2)-C(4)	110.6 (2)	C(6)-N(2)-C(4)	112.9 (2)

Table 6
Hydrogen-bonding geometry (Å, °) for (tmenH$_2$)[MoS$_4$] **2**

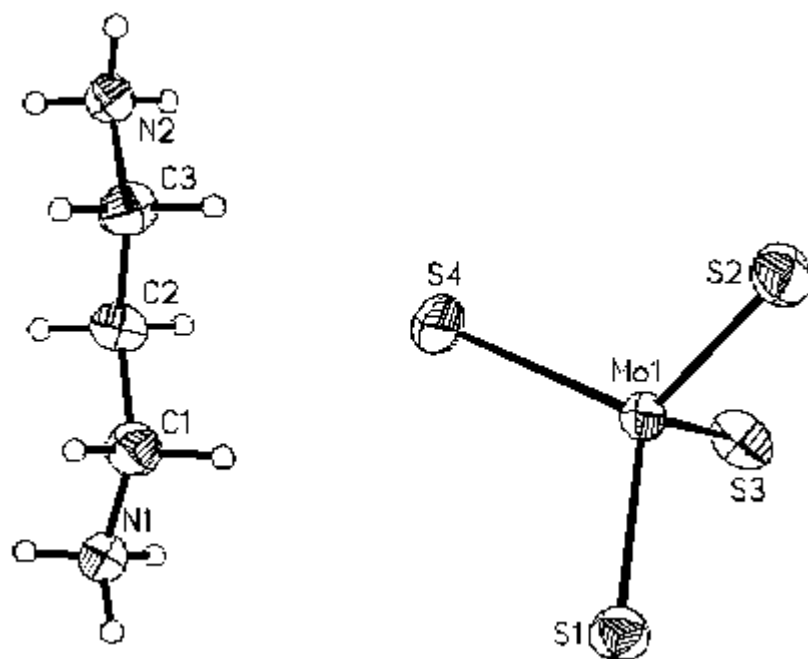| D-H…A	d(D-H)	d(H…A)	d(D…A)	<DHA	Symmetry code
N1-H1⋯S1	0.910	2.567	3.267	134.21	
N1-H1⋯S2	0.910	2.757	3.504	140.09	
N2-H1⋯S3	0.910	2.740	3.394	129.62	–x+1, -y+1, -z+1
N2-H1⋯S2	0.910	2.776	3.551	143.82	–x+1, -y+1, -z+1

D = Donor; A = Acceptor

Figure 1

Crystal structure of the anion and cation in $(1,3\text{-pnH}_2)[MoS_4]$ **1** with labelling and displacement ellipsoids drawn at the 50% probability level.
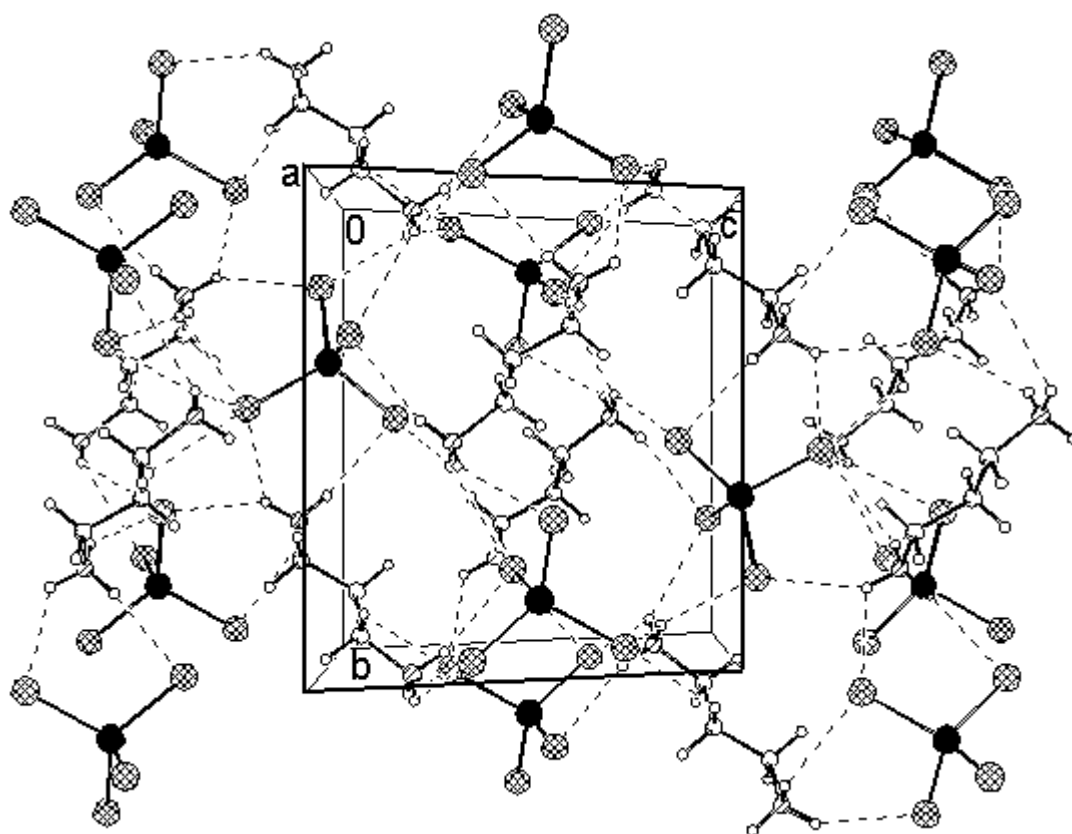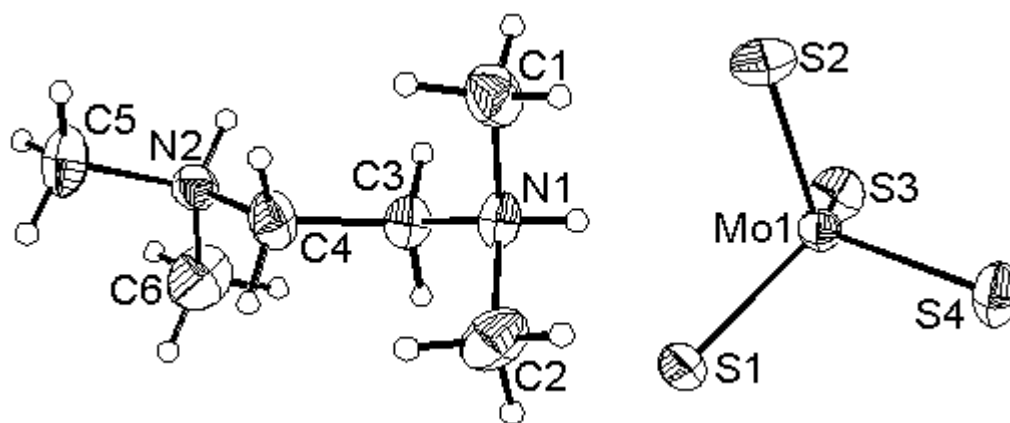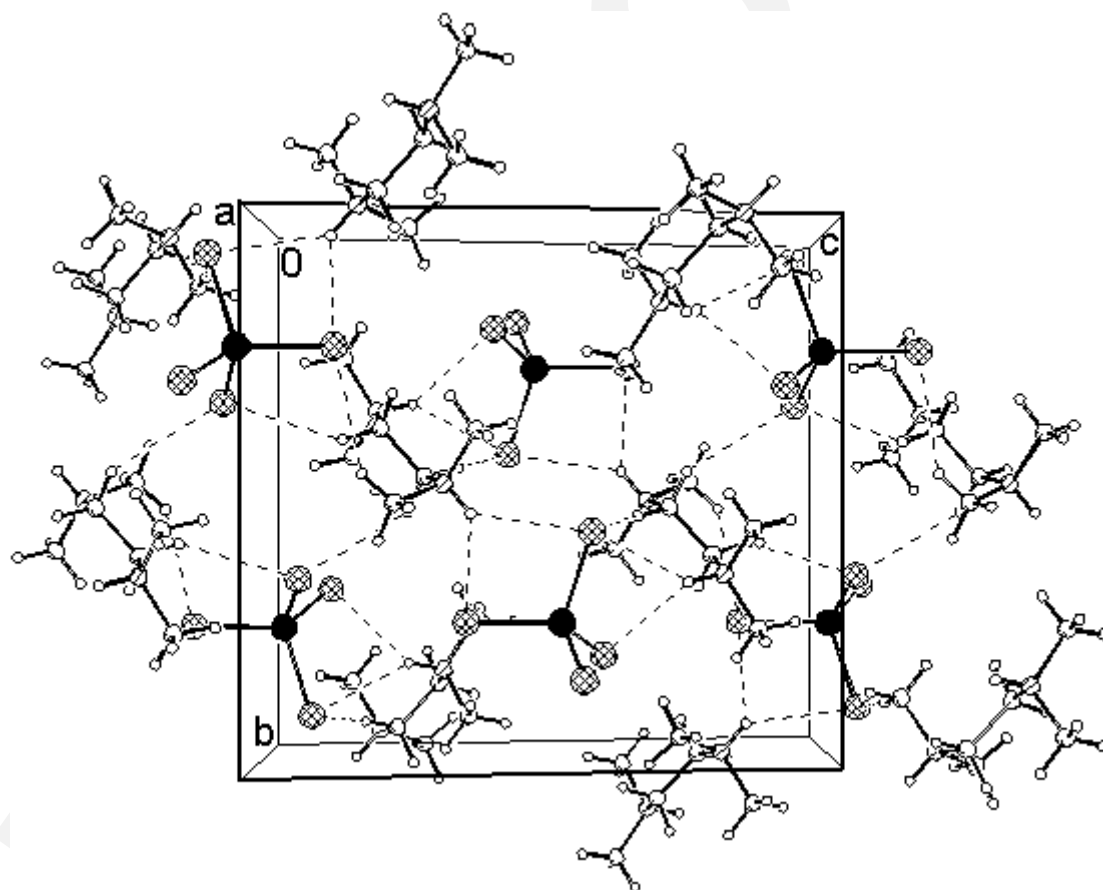
Figure 2

Crystal structure of (1,3-pnH$_2$)[MoS$_4$], **1** with view along the a-axis (hydrogen bonding is shown as dashed lines).

Figure 3

Crystal structure of the anion and cation in (tmenH$_2$)[MoS$_4$], **2** with labelling and displacement ellipsoids drawn at the 50% probability level.

Figure 4

Crystal structure of the anion and cation in (tmenH$_2$)[MoS$_4$], **2** with view along the a-axis (hydrogen bonding is shown as dashed lines).
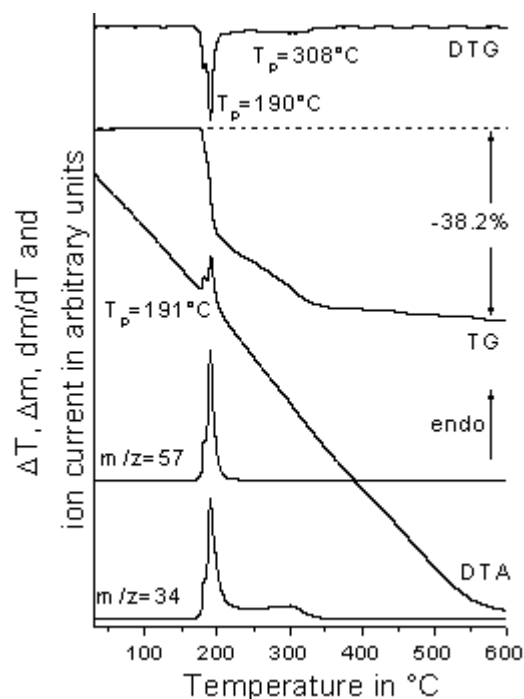
Figure 5

DTA, TG, DTG and MS trend scan curves for compound **1** (weight: 22.40 mg; heating rate: 4°C/min.; m/z = 57 (fragment of 1,3-propanediamine); m/z = 34 (H_2S); T_p = peak temperature).
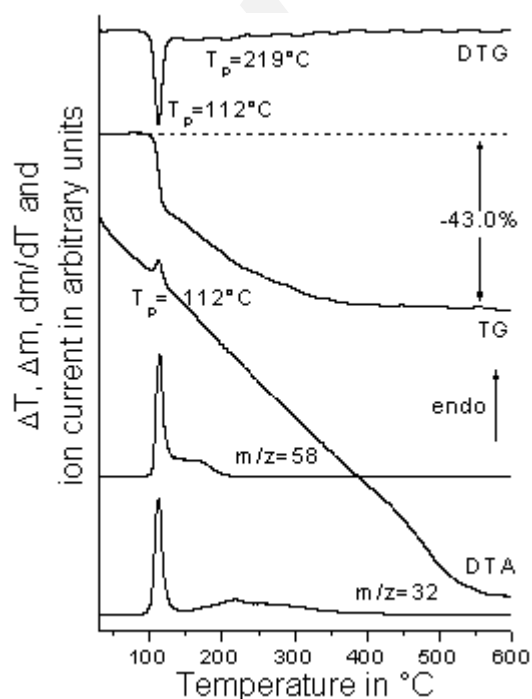

Figure 6

DTA, TG, DTG and MS trend scan curves for compound **2** (weight: 19.20 mg; heating rate: 4°C/min.; m/z = 58 (fragment of N,N,N',N'-tetramethylethylene-diamine); m/z = 34 (H_2S); T_p = peak temperature).