

Crystallographic and thermal investigations of organic ammonium tetrathiomolybdates

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Dedicated to Prof. P.T. Manoharan on the occasion of his 72nd birthday

Abstract

The organic ammonium tetrathiomolybdates *N*-methylethylenediammonium tetrathiomolybdate (*N*-Me-enH₂)[MoS₄] (**1**), *N*-(3-aminopropyl)propane-1,3-diaminium tetrathiomolybdate (dipnH₂)[MoS₄] (**2**), 4-(2-ammonioethyl)piperazin-1-ium tetrathiomolybdate hemihydrate (2-pipH-1-EtNH₃)[MoS₄] · 1/2H₂O (**3**) and 2,2'-iminodiethanaminium tetrathiomolybdate (dienH₂)[MoS₄] (**4**), were synthesized by an aqueous reaction of ammonium tetrathiomolybdate with the organic amines *N*-methylethylenediamine (*N*-Me-en), bis(3-aminopropyl)amine (dipn), 2-piperazin-1-ylethanamine (2-pip-1-EtNH₂) and bis(2-aminoethyl)amine (dien), respectively. All compounds were characterized by elemental analysis, ¹H NMR, IR, Raman and UV–Vis spectra, and the crystal structures of compounds **1–3** were determined. The structures of **1–3** consist of diprotonated organic cations, which are linked to the tetrahedral [MoS₄]²⁻ anions with the aid of several weak H-bonding interactions. The MoS₄ tetrahedron in all compounds is slightly distorted with one or more Mo–S bonds being elongated, which can be attributed to the H-bonding interactions. The difference Δ between the longest and the shortest Mo–S bond lengths for **1–3** are 0.0379, 0.0186 and 0.0302 Å, respectively. Unlike **1** and **2**, which are anhydrous, compound **3** is a hemihydrate. The water molecule in **3** occupies the pores between alternating layers of the cations and anions in the crystallographic *bc*-plane. Compound **3** exhibits four types of weak H-bonding interactions namely N–H···S, N–H···O, O–H···S and C–H···S. All four tetrathiomolybdates decompose endothermically forming amorphous disulfides containing C and N. A comparative structural description of 28 tetrathiomolybdates is presented. © 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

The chemistry of tetrathiomolybdate is an area of current research interest in view of its usefulness as a precursor for the preparation of catalytically active metal sulfide materials [1]. A very important application is the routine use as a starting material in synthetic inorganic chemistry for the preparation of several Mo–S compounds [2,3]. In organic syntheses, tetrathiomolybdate has been used as a S-transfer reagent for the synthesis of several organo sulfur

compounds [4]. The reactivity of tetrathiomolybdate has been investigated with several organic agents like alkyl halides [5], organic trisulfide [6] organic disulfide [7], thiophenol [8], 1,1-dithiolate disulfide [9], and more recently with organic amines [10–17]. Unlike the reactions of tetrathiomolybdate with other organic reagents like organic disulfides or thiophenol where the tetrathiomolybdate undergoes changes like for example the reduction of Mo(VI) to Mo(V), with organic amines the tetrahedral tetrathiomolybdate(VI) core is retained intact and the organic amines function as cations for charge balance [10–16]. From a structural point of view the acentric tetrahedral [MoS₄]²⁻ unit can be used as a building block

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to create non-centrosymmetric materials by an appropriate choice of counter cations, which can also be used as cationic handles to distort the MoS_4 tetrahedron by suitably altering the cation–anion interactions. In this context we are investigating the structural chemistry of group VI tetrathiomolybdates, and for tetrathiotungstates we have demonstrated that the reaction of $[\text{WS}_4]^{2-}$ with organic amines leads to the facile formation of organic ammonium tetrathiotungstates [15,18–24]. In many of these structurally characterized compounds, the WS_4 tetrahedron is slightly distorted with one or two of the W–S bonds elongated, which has been attributed to the $\text{S} \cdots \text{H}$ interactions between $[\text{WS}_4]^{2-}$ and the organic cation [21–25]. The importance of H-bonding interactions in the structural chemistry of tetrathiotungstates can also be evidenced by the fact that in some compounds the organic amines are only partially protonated. In view of this, it is of interest to investigate the reactions of tetrathiomolybdates with tri- or polyamines and alkyl substituted amines. In the present work, we have studied the reaction of $[\text{MoS}_4]^{2-}$ with the methyl substituted organic amine *N*-methylethylenediamine (*N*-Me-en) and three triamines bis(3-aminopropyl)amine (dipn), 2-piperazin-1-ylethanamine (2-pip-1-EtNH₂) and bis(2-aminoethyl)amine (dien). Herein we describe the synthesis, spectroscopic, and thermal characterization of the organic tetrathiomolybdates obtained by the above reaction. The structures of compounds **1–3** are reported here, while the structure of **4** has been reported by Pokrel et al. earlier [26]. Compounds **1–3** constitute new additions to the growing list of structurally characterized tetrathiomolybdates. The availability of structural information for several tetrathiomolybdates permits us to make a comparative study of the structural features, the details of which are described in this paper.

2. Experimental

2.1. Materials and physical measurements

The amines *N*-methylethylenediamine (*N*-Me-en), bis(3-aminopropyl)amine (dipn), 2-piperazinyl-1-ethylamine (2-pip-1-EtNH₂), bis(2-aminoethyl)amine (dien), and the solvents were used as obtained from commercial sources with analytical purity. $(\text{NH}_4)_2[\text{MoS}_4]$ (ATM) was prepared by a literature method [27]. The details of the instrumentation used for the elemental analysis, IR, Raman and UV–Vis spectroscopy, thermal analysis were the same as described in our previous reports [11,12]. X-ray powder patterns were recorded in transmission geometry using a STOE STADI P diffractometer ($\text{Cu K}\alpha = 1.54056 \text{ \AA}$).

2.2. Preparation of compounds **1–4**

Freshly prepared ATM (260 mg, 1 mmol) was dissolved in 15 mL of distilled water containing 2 drops of 25% aqueous ammonia, and filtered. To the deep red coloured filtrate, *N*-Me-en (0.3 mL, 3.4 mmol) was added in drops at room temperature and the reaction mixture was left aside

for crystallisation. After 1–2 days, red blocks of compound **1** slowly crystallized from the solution. The crystals were isolated by filtration, washed with a little ice-cold water (2 mL) followed by isopropanol (10 mL) and ether (10 mL) and dried under vacuum. Yield 75%. The use of dipn, 2-pip-1-EtNH₂ and dien instead of *N*-Me-en in above synthesis afforded the complexes **2–4** in 70% yield. All complexes are quite stable in air and dissolve in aqueous alkali solution, DMSO and DMF.

(*N*-Me-enH₂)[MoS₄] (**1**): *Anal.* Calc. for $\text{C}_3\text{H}_{12}\text{N}_2\text{MoS}_4$: C, 9.28; H, 3.12; N, 6.88; S, 33.04. Found: C, 9.34; H, 3.11; N, 6.88; S, 33.89%.

IR data: 3046, 2955, 2727, 1567, 1527, 1466, 1442, 1412, 1203, 1116, 1051, 1025, 935, 824, 766, 496, 478 (ν_3), 460 (ν_3), 448 (ν_1), 433, 254, 166, 131, 99 cm^{-1} ; Raman data: 475 (ν_3), 458 (ν_3), 449 (ν_1), 412, 202, 185, 170 cm^{-1} .

UV–Vis data (aqueous ammonia): 468, 317, 245 nm.

¹H NMR (DMSO-*d*₆): δ 2.59 (s, 3H), 3.12 (t, 2H, $J = 5 \text{ Hz}$), 3.09 (t, 2H, $J = 5 \text{ Hz}$) ppm.

(dipnH₂)[MoS₄] (**2**): *Anal.* Calc. for $\text{C}_6\text{H}_{19}\text{N}_2\text{MoS}_4$: C, 20.16; H, 5.37; N, 11.76; S, 35.88. Found: C, 20.15; H, 5.29; N, 11.57; S, 35.86%.

IR data: 3272, 3228, 2998, 1575, 1519, 1461, 1380, 1284, 1083, 989, 755, 477 (ν_3), 453 (ν_1), 219, 262, 194 cm^{-1} ; Raman data: 475 (ν_3), 453 (ν_1), 189 (ν_4), 178 cm^{-1} .

UV–Vis data (aqueous ammonia): 468, 317, 241 nm.

¹H NMR (DMSO-*d*₆): δ 1.65 (p, 2H, $J = 7 \text{ Hz}$), 2.57 (t, 2H, $J = 7 \text{ Hz}$), 2.81 (t, 2H, $J = 7 \text{ Hz}$) ppm.

(2-pipH-1-EtNH₃)[MoS₄] · 1/2H₂O (**3**): *Anal.* Calc. for $\text{C}_6\text{H}_{18}\text{N}_3\text{MoS}_4\text{O}_{0.5}$: C, 19.77; H, 4.98; N, 11.53; S, 35.19. Found: C, 19.62; H, 4.89; N, 11.39; S, 35.38%.

IR data: 3434, 3162, 3081, 2950, 1635, 1608, 1553, 1451, 1367, 1172, 1094, 1067, 993, 902, 509, 475 (ν_3), 451 (ν_1), 435, 363, 335, 279, 227, 202 (ν_4), 173, 139, 105, 88 cm^{-1} ; Raman data: 477 (ν_3), 466 (ν_3), 451 (ν_1), 189, 179, 172, 110 cm^{-1} .

UV–Vis data (aqueous ammonia): 468, 317, 239 nm.

¹H NMR (DMSO-*d*₆): δ 2.57 (t, 4H, $J = 5 \text{ Hz}$), 3.07 (t, 4H, $J = 5 \text{ Hz}$), 2.89 (t, 2H, $J = 6 \text{ Hz}$), 2.40 (t, 2H, $J = 6 \text{ Hz}$) ppm.

(dienH₂)[MoS₄] (**4**): *Anal.* Calc. for $\text{C}_4\text{H}_{15}\text{N}_3\text{MoS}_4$: C, 14.58; H, 4.60; N, 12.76; S, 38.94. Found: C, 14.65; H, 4.56; N, 12.67; S, 38.87%.

IR data: 3257, 3054 (br), 1568, 1540, 1504, 1464, 1459, 1365, 1345, 1311, 1283, 1257, 1188, 1177, 1088, 1054, 1027, 987, 959, 932, 866, 838, 818, 797, 770, 676, 495, 464 (ν_3), 427, 320, 283, 204 (ν_4), 185 (ν_2), 171, 141, 125, 92 cm^{-1} ; Raman data: 491, 479 (ν_3), 469 (ν_3), 451 (ν_1), 192 (ν_4), 182 cm^{-1} .

UV–Vis data (aqueous ammonia): 468, 317, 240 nm.

¹H NMR (DMSO-*d*₆): δ 2.82 (t, 2H, $J = 5.4 \text{ Hz}$), 2.66 (t, 2H, $J = 5.54 \text{ Hz}$) ppm.

2.3. Crystal structure determination

Single crystal X-ray work was performed using a AED-II 4-circle diffractometer from STOE & CIE ($\text{Mo K}\alpha$ radiation; $\lambda = 0.71073 \text{ \AA}$). The raw intensities were corrected

Table 1
Technical details of data acquisition and selected refinement results for 1–3

Compound	1	2	3
Formula	C ₃ H ₁₂ N ₂ S ₄ Mo	C ₆ H ₁₉ N ₃ S ₄ Mo	C ₆ H ₁₈ N ₃ S ₄ MoO _{0.5}
Temperature (K)	293	293	293
Wavelength (pm)	71.073	71.073	71.073
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Pca</i> 2 ₁	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	7.8805(11)	13.7377(13)	24.451(3)
<i>b</i> (Å)	11.8098(16)	7.4901(7)	7.1150(10)
<i>c</i> (Å)	11.9492(17)	13.4526(11)	17.864(2)
β (°)			115.030(10)
Volume (Å ³)	1112.1(3)	1384.2(2)	2815.9(6)
<i>Z</i>	4	4	8
μ [mm ⁻¹]	1.874	1.522	1.501
<i>F</i> (000)	600	728	1480
Molecular weight (g/mol)	300.33	357.42	364.41
<i>D</i> _{calc} (g cm ⁻³)	1.794	1.715	1.719
Crystal size (mm)	0.14 0.12 0.10	0.2 0.18 0.16	0.12 0.09 0.07
<i>hkl</i> Range	–11/1; –16/1; –16/1	–19/2; –10/1; –18/6	0/34; –1/10; –25/22
2 θ Range (°)	4.84–60.08	5.44–60.04	3.68–60.06
Reflections collected	2227	4107	4833
Reflections unique	2141	2959	4095
Data (<i>F</i> _o > 4 σ (<i>F</i> _o))	1632	2385	3008
<i>R</i> _{int}	0.0367	0.0404	0.0223
Minimum/maximum transmission	0.7214/0.8381	0.7029/0.8501	0.7075/0.8530
$\Delta\rho$ (e Å ⁻³)	–0.731/0.625	–0.568/0.574	–0.445/0.426
Parameters	93	129	134
<i>R</i> ₁ [<i>F</i> _o > 4 σ (<i>F</i> _o)]	0.0305	0.0295	0.0285
<i>W</i> <i>R</i> ₂ for all unique data	0.0699	0.0700	0.0684
Flack <i>x</i> -parameter	–0.05(8)	–0.07(6)	
Goodness of fit	1.006	1.028	0.985

for Lorentz, polarization effects and a numerical absorption correction was applied for all compounds. The structures of the compounds 1–3 were solved with direct methods using SHELXS-97 [28] and refinement was done against *F*² using SHELXL-97 [28]. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were located in difference map but in most cases were positioned with idealized geometry (ammonium hydrogen atoms in 2 and 3 allowed to rotate but not to tip) and refined isotropically using a riding model. The H atom of the water in 3 was located in difference map, its bond lengths set to ideal values and afterwards it was refined using a riding model. The absolute structure for 1 and 2 was determined and is in agreement with selected setting. The technical details of data acquisition and some selected refinement results for 1–3 are summarised in Table 1.

3. Results and discussion

3.1. Synthesis

Compounds 1–4 were synthesized by a direct aqueous reaction of ATM with the corresponding organic amine. In this reaction the stronger organic bases displace the weaker ammonia from ATM and no change is observed with respect to the tetrathiomolybdate. This observation is in accordance with the known stability of [MoS₄]²⁻ in alkaline medium [29,30]. The compounds analysed satisfac-

torily for the proposed formula containing [MoS₄]²⁻ in association with the diprotonated cations of *N*-Me-en, dipn, 2-pip-1-EtNH₂ and dien in 1–4, respectively. The presence of the organic amine and [MoS₄]²⁻ could be inferred based on the NMR and UV–Vis spectral data, respectively. In earlier reports we have shown that the use of the cyclic diamine (\pm)*trans*-1,2-diaminocyclohexane (*trans*-1,2-cn) results in the formation of (*trans*-1,2-cnH₂)₂[MoS₄] containing the monoprotated amine [14] while the use of the polyamine tris(2-aminoethylamine) (tren) leads to the formation of (trenH₂)₂[MoS₄]·H₂O [11]. The synthesis of compound 4 containing the diprotonated triamine dien has been reported earlier by an alternate method which involves passing of H₂S gas into an aqueous molybdate solution containing dien [26]. It is interesting to note that the central secondary amine functionality and one of the terminal N atoms of the triamine bis(3-aminopropyl)amine (dipn) are protonated in 2 unlike in the related triamine dien in 4 where the protonation of the terminal primary amine groups has been reported [26]. In 3 only two of the N atoms are protonated. It has been reported that MoO₃ dissolves in aqueous dien resulting in the formation of the hexacoordinated neutral complex [MoO₃(dien)] where dien functions as a neutral tridentate ligand [31,32]. The neutral compound is freely soluble in water and forms (dienH₂)₂[MoO₄] in solution [33]. While (dienH₂)₂[MoO₄] exists only in solution, the corresponding tetrathio analogue 4 can be crystallised as a stable solid indicating the difference in the chemistry of

oxo- and thiomolybdates. Our several efforts to prepare the neutral trithio complex $[\text{MoS}_3(\text{dien})]$ by the reaction of MoS_3 with dien were not successful as MoS_3 does not dissolve in aqueous dien unlike MoO_3 . Furthermore, our attempts to obtain a 2:3 $[\text{MoS}_4]^{2-}$ complex of the fully protonated dipn and dien by changing the reaction stoichiometries were not successful. In all cases only the diprotonated ammonium compounds were obtained. As observed earlier [12] for other organic thiomolybdates, the aqueous reaction of **1–4** with $[\text{Ni}(\text{en})_3]^{2+}$ resulted in a cation exchange leading to the quantitative formation of the known metal-organic tetrathiomolybdate $[\text{Ni}(\text{en})_3][\text{MoS}_4]$ [34].

3.2. Crystal structure description of **1–3**

Compound **1** ($N\text{-Me-enH}_2$)[MoS_4] crystallises in the non-centrosymmetric orthorhombic space group $P2_12_12_1$ with all atoms located in general positions and its structure consists of tetrahedral $[\text{MoS}_4]^{2-}$ dianions and N -methyl-ethylenediammonium cations (Fig. 1). Compound **1** is isostructural with the corresponding W analogue [22] in accordance with our earlier observation wherein a pair of $[\text{MS}_4]^{2-}$ ($M = \text{Mo}, \text{W}$) compounds linked to the same cation are isostructural. The MoS_4 tetrahedron is slightly distorted and the S–Mo–S bond angles range between $108.36(6)^\circ$ and $110.65(5)^\circ$ (average: 109.47°) (Table 2). The Mo–S distances vary from 2.1635(14) to 2.2014(12) Å with a mean Mo–S bond length of 2.1861 Å. An analysis of the crystal structure reveals that

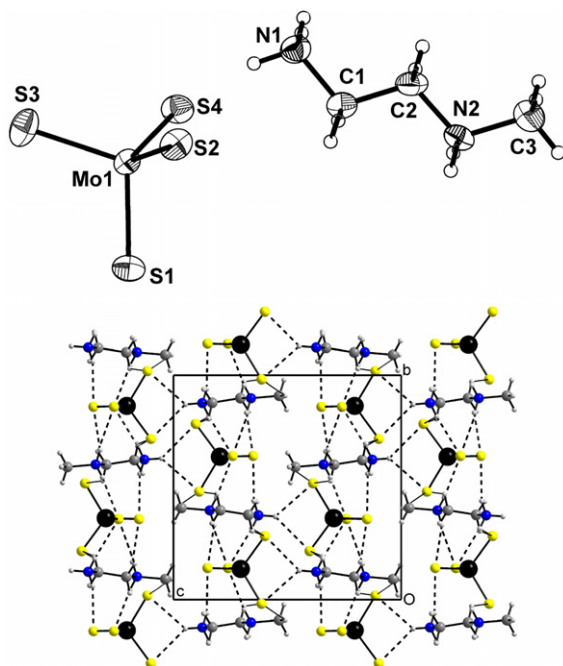


Fig. 1. The crystal structure of ($N\text{-Me-enH}_2$)[MoS_4] (**1**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius (top). A view of the packing diagram of **1** along a -axis (bottom). Hydrogen bonding is shown as dashed lines.

Table 2
Selected geometric parameters (Å, °) for compounds **1–3**

$(N\text{-Me-enH}_2)[\text{MoS}_4]$ (1)			
Mo(1)–S(2)	2.1635(14)	Mo(1)–S(3)	2.1997(13)
Mo(1)–S(4)	2.1798(14)	Mo(1)–S(1)	2.2014(12)
S(2)–Mo(1)–S(4)	110.65(5)	S(2)–Mo(1)–S(1)	109.37(6)
S(2)–Mo(1)–S(3)	108.36(6)	S(4)–Mo(1)–S(1)	108.91(5)
S(4)–Mo(1)–S(3)	109.78(6)	S(3)–Mo(1)–S(1)	109.76(5)
$(\text{dipnH}_2)[\text{MoS}_4]$ (2)			
Mo(1)–S(1)	2.1717(13)	Mo(1)–S(4)	2.1844(14)
Mo(1)–S(3)	2.1810(10)	Mo(1)–S(2)	2.1903(9)
S(1)–Mo(1)–S(3)	108.97(5)	S(1)–Mo(1)–S(2)	109.72(5)
S(1)–Mo(1)–S(4)	109.30(6)	S(3)–Mo(1)–S(2)	110.33(4)
S(3)–Mo(1)–S(4)	109.44(5)	S(4)–Mo(1)–S(2)	109.07(5)
$(2\text{-pipH-1-EtNH}_3)[\text{MoS}_4] \cdot 1/2\text{H}_2\text{O}$ (3)			
Mo(1)–S(4)	2.1703(7)	Mo(1)–S(2)	2.1884(7)
Mo(1)–S(3)	2.1750(7)	Mo(1)–S(1)	2.2005(8)
S(4)–Mo(1)–S(3)	109.43(3)	S(4)–Mo(1)–S(1)	108.51(3)
S(4)–Mo(1)–S(2)	110.34(3)	S(3)–Mo(1)–S(1)	110.29(3)
S(3)–Mo(1)–S(2)	108.82(3)	S(2)–Mo(1)–S(1)	109.45(3)

the each $[\text{MoS}_4]^{2-}$ anion is linked to four different cations with the aid of several weak $\text{N–H} \cdots \text{S}$ and $\text{C–H} \cdots \text{S}$ interactions (Table 3). A total of seven $\text{N–H} \cdots \text{S}$ interactions ranging from 2.362 to 2.868 Å and four $\text{C–H} \cdots \text{S}$ interactions between 2.825 and 2.953 Å are observed and all $\text{S} \cdots \text{H}$ contacts are shorter than the sum of their van der Waals radii [35]. The two longer $\text{Mo–S}(3)$ and $\text{Mo–S}(1)$ bonds at 2.2014(12) and 2.1997(13) Å are involved in shorter $\text{N–H} \cdots \text{S}$ contacts accompanied by larger N–H–S angles while the other two shorter Mo–S bonds are involved in longer $\text{S} \cdots \text{H}$ contacts. Thus the strength and number of the $\text{S} \cdots \text{H}$ interactions can account for the observed distinct Mo–S bond distances. The three-dimensional H-bonded network is shown in Fig. 1. The difference Δ between the longest and shortest Mo–S bond lengths in **1** is 0.0379 Å and is quite larger than the Δ value of 0.0111 Å observed earlier (enH_2)[MoS_4] [10] (enH_2 is ethylenediammonium).

Compound **2** (dipnH_2)[MoS_4], crystallises in the non-centrosymmetric orthorhombic space group $Pca2_1$ with all atoms located in general positions. The structure consists of diprotonated (dipnH_2) $^{2+}$ cations and $[\text{MoS}_4]^{2-}$ anions (Fig. 2). The geometric parameters of the cation are in the normal range. Compound **2** is isostructural to its corresponding W analogue [23] and one of the primary N atoms and the central secondary N atoms are protonated. The MoS_4 tetrahedron is slightly distorted (S–Mo–S angles: $108.97(5)$ – $110.33(4)^\circ$; average: 109.47°) with Mo–S bond distances ranging from 2.1717(13) to 2.1903(9) Å (average: 2.1818 Å) (Table 2). The observed Δ value of 0.0186 Å, is less than that for compound **1**. Cations and anions are involved in three varieties of H-bonding interactions, which include eight $\text{N–H} \cdots \text{S}$, one $\text{N–H} \cdots \text{N}$ and four $\text{C–H} \cdots \text{S}$ bonds (Table 4). The resulting three-dimensional crystal-packing diagram is displayed in Fig. 2. (dipnH_2) $^{2+}$ and $[\text{MoS}_4]^{2-}$ are stacked in rods along

Table 3
Hydrogen-bonding geometry (Å, °) for (N-Me-enH₂)[MoS₄] (1)

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA	Symmetry code
N1–H1N1···S3	0.890	2.418	3.254	156.56	$-x + 3/2, -y + 1, z + 1/2$
N1–H2N1···S4	0.890	2.663	3.368	136.84	
N1–H2N1···S2	0.890	2.746	3.411	132.57	
N1–H3N1···S1	0.890	2.442	3.280	157.13	$x + 1/2, -y + 1/2, -z + 1$
N1–H3N1···S4	0.890	2.868	3.388	118.84	$x + 1/2, -y + 1/2, -z + 1$
N2–H1N2···S3	0.900	2.362	3.190	152.89	$x - 1/2, -y + 1/2, -z + 1$
N2–H2N2···S1	0.900	2.377	3.225	157.12	$-x + 1/2, -y + 1, z + 1/2$
C1–H1A···S4	0.970	2.952	3.583	123.8	$x - 1/2, -y + 1/2, -z + 1$
C2–H2A···S1	0.970	2.953	3.719	136.6	$x + 1/2, -y + 1/2, -z + 1$
C2–H2B···S2	0.970	2.939	3.530	120.4	$-x + 3/2, -y + 1, z + 1/2$
C3–H3A···S2	0.960	2.825	3.531	131.0	$-x + 1/2, -y + 1, z + 1/2$

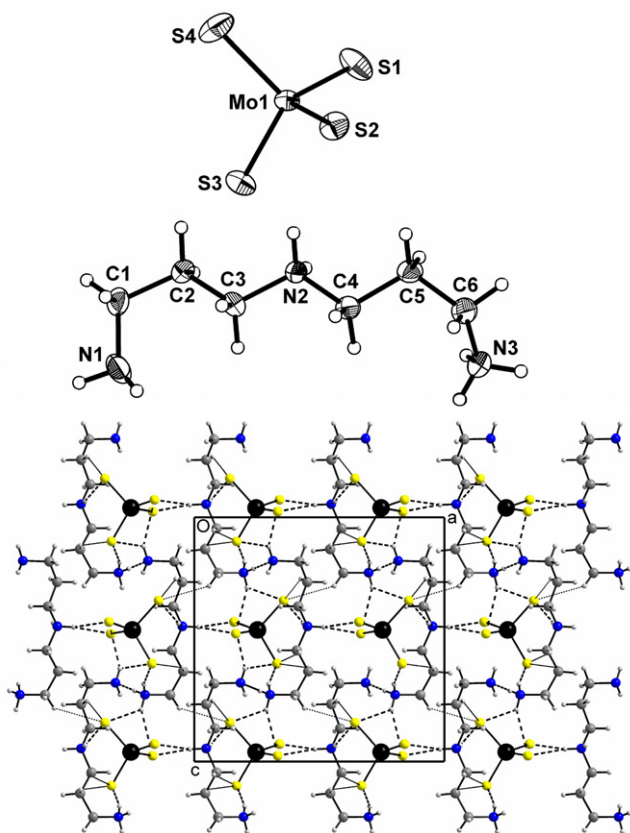


Fig. 2. The crystal structure of (dipnH₂)[MoS₄] (2) showing the atom-labelling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius (top). The three-dimensional extended network with view along *b*-axis (bottom). H-bonding is shown as dashed lines.

[001] to form a pseudo-hexagonal array. The cations and anions alternate along [100] and [010]. In the (010) plane a layer like arrangement is found with the anions being located in the pockets formed by three neighboring cations. A very short N3–H···N1 contact at 1.864 Å links the cations into a chain along the '*c*'-axis and each anion is surrounded by four cations and vice versa.

Compound 3 (2-pipH-1-EtNH₃)[MoS₄]·1/2H₂O (3), crystallises in the monoclinic space group *C2/c* and its structure consists of (2-pipH-1-EtNH₃)²⁺, [MoS₄]²⁻

located in general position and a crystal water with the oxygen located on a twofold axis (Fig. 3). The cyclic amine adopts the chair conformation with the ethylammonium group occupying equatorial position and the tertiary N remains unprotonated. The geometric parameters of the organic cation are in the normal range. Like for the other two compounds, the [MoS₄] tetrahedron is slightly distorted (S–Mo–S: 108.51 (3)–110.34 (3)°; Mo–S bond lengths: 2.1703 (7)–2.2005 (8) Å; average Mo–S distance: 2.1835 Å) (Table 2). The difference between the longest and shortest Mo–S distance Δ is 0.0302 Å and is comparatively larger than that for 2 but less than that observed in 1. (2-pipH-1-EtNH₃)²⁺, [MoS₄]²⁻, and H₂O are linked via four varieties of H-bonding interactions consisting of five N–H···S, one N–H···O, one O–H···S and one C–H···S bonds (Table 5). It is interesting to note that the crystal water is H-bonded to two symmetry related [MoS₄]²⁻ anions via O–H···S bonds while O11 forms H-acceptor bonds (N–H···O) with the organic cation leading to a tetrahedral coordination around the oxygen of water (Fig. 4). This unit linked via H₂O can be considered as a synthon to describe the extended supramolecular structure which consists of alternating layers of organic cations and anions with the water molecules occupying the pores between the alternating layers. The N–H···S and C–H···S interactions serve to link the layers of cations and anions (Fig. 4).

3.3. Spectral studies

Compounds 1–4 were characterised by using a combination of ¹H NMR, UV–Vis, infrared and Raman spectroscopic techniques. The observed chemical shifts (see Section 2) are in the normal range confirming the presence of the organic moieties in 1–4. The electronic spectra of 1–4 recorded in dilute ammonia exhibit intense signals at around 468, 317 and 241 nm and the peak positions are identical within experimental error to ammonium tetrathiomolybdate [27]. These bands can be assigned to the charge transfer transitions of the [MoS₄]²⁻ anion. The signals in the mid IR (up to 500 cm⁻¹) originate from the organic cations, while the vibrations of the [MoS₄]²⁻ unit are observed at lower energies below 500 cm⁻¹. As expected the IR spectra of compounds 1, 2 and 4 are

Table 4
Hydrogen-bonding geometry (Å, °) for (dipnH₂)[MoS₄] (2)

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠DHA	Symmetry code
N1–H2N1···S3	0.890	2.759	3.563	150.77	$-x + 1, -y + 2, z - 1/2$
N1–H2N1···S1	0.890	2.768	3.345	123.78	$-x + 1, -y + 2, z - 1/2$
N2–H1N2···S3	0.900	2.645	3.384	140.06	
N2–H1N2···S2	0.900	2.711	3.415	135.78	
N2–H2N2···S4	0.900	2.627	3.479	158.30	$x - 1/2, -y + 1, z$
N3–H1N3···N1	0.890	1.864	2.752	175.07	$-x + 1/2, y, z + 1/2$
N3–H2N3···S2	0.890	2.648	3.451	150.60	$-x + 1, -y + 1, z + 1/2$
N3–H2N3···S4	0.890	2.890	3.510	128.08	$-x + 1, -y + 1, z + 1/2$
N3–H3N3···S1	0.890	2.553	3.401	159.37	$x - 1/2, -y + 1, z$
C2–H2A···S4	0.970	2.837	3.675	145.16	$x - 1/2, -y + 1, z$
C4–H4B···S1	0.970	2.933	3.775	145.79	$x - 1/2, -y + 2, z$
C5–H5A···S1	0.970	2.808	3.638	144.03	$x - 1/2, -y + 1, z$
C6–H6A···S4	0.970	2.922	3.614	129.16	$-x + 3/2, y, z + 1/2$

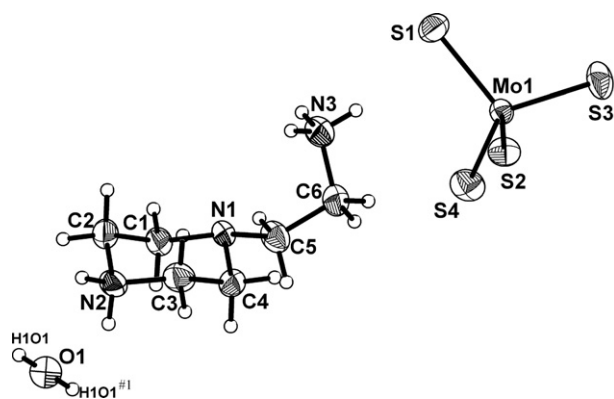


Fig. 3. Crystal structure of (2-pipH-1-EtNH₃)[MoS₄] · 1/2H₂O (3) showing the atom-labelling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. Symmetry code: #1 1 – *x*, *y*, 1.5 – *z*.

identical with that of their W counterparts [22,23] with the signals due to the vibrations of [MoS₄]^{2–} unit occurring at slightly higher energies. The strong band at 3434 cm^{–1}, which can be assigned to the O–H stretching vibration indicates the presence of water in the hemihydrate compound 3. For all compounds the N–H region appears broad and shifted to lower wave numbers as compared to the free amines. This can be attributed to the change of amine group into the ammonium cation and the hydrogen bonding interactions between the organic cation and [MoS₄]^{2–}

anion. A broad signal due to the N–H vibration occurs at around 3046 cm^{–1} for 1 while for 2–4, this vibration occurs at 2998, 3081 and 3054 cm^{–1}, respectively. However, the N–H region of 2 and 4 is quite different from that of 1, as extra bands at 3272, 3228 cm^{–1} in 2 and 3257 cm^{–1} in 4, are observed. These signals can be attributed to the N–H vibrations of the free amine part of the organic cations in 2–4, indicating that the amines are partially protonated in 2–4. Such signals have been earlier observed for the free amine functionality in (trenH₂)[MoS₄] · H₂O [11]. For the free tetrahedral [MoS₄]^{2–} anion four characteristic bands ν_1 (A₁), ν_2 (E), ν_3 (F₂), and ν_4 (F₂) are expected [36,37]. All four bands are Raman active while only ν_3 and ν_4 are infrared active. When the *T_d* symmetry of MoS₄ is lowered to *C_{2v}* as in [Ni(MoS₄)₂]^{2–} where [MoS₄]^{2–} functions as a bidentate ligand, a splitting of the triply degenerate ν_3 (F₂) vibration of the M–S bond occurs [36,37]. In [Ni(MoS₄)₂]^{2–} the Mo–S bond to the bridging S atom is long (Mo–S–Ni) and the Mo–S bond to terminal S atom is short (2.151 Å). In our compounds the longer Mo–S bonds are always observed when strong S···H bonding interactions are present, and the Mo–S bond length distribution indicates a slight distortion of the tetrahedra. In 1 the asymmetric stretching vibration ν_3 appears as a split signal at 463 and 448 with a further shoulder at 433 cm^{–1}. The observed extra signals can be attributed to the distortion of MoS₄ tetrahedron and lowering of symmetry. All compounds exhibit a strong signal

Table 5
Hydrogen-bonding geometry (Å, °) for (2-pipH-1-EtNH₃)[MoS₄] · 1/2H₂O (3)

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠DHA	Symmetry code
N2–H1N2···O1	0.900	2.349	3.064	136.29	
N2–H1N2···S2	0.900	2.706	3.445	140.07	$-x + 3/2, y + 1/2, -z + 3/2$
N2–H2N2···S3	0.900	2.451	3.282	153.64	$x - 1/2, y + 1/2, z$
N3–H1N1···S2	0.890	2.529	3.320	148.39	$-x + 3/2, -y + 1/2, -z + 1$
N3–H2N2···S1	0.890	2.558	3.415	161.85	
N3–H3N3···S1	0.890	2.714	3.378	132.31	$-x + 3/2, -y + 3/2, -z + 1$
O1–H101···S4	0.820	2.670	3.443	157.88	$x - 1/2, y - 1/2, z$
C2–H2A···S3	0.970	2.856	3.773	158.05	$-x + 3/2, -y + 3/2, -z + 1$
C5–H5A···S1	0.970	2.826	3.614	138.93	$-x + 3/2, -y + 1/2, -z + 1$
C6–H6A···S4	0.970	2.975	3.598	123.15	

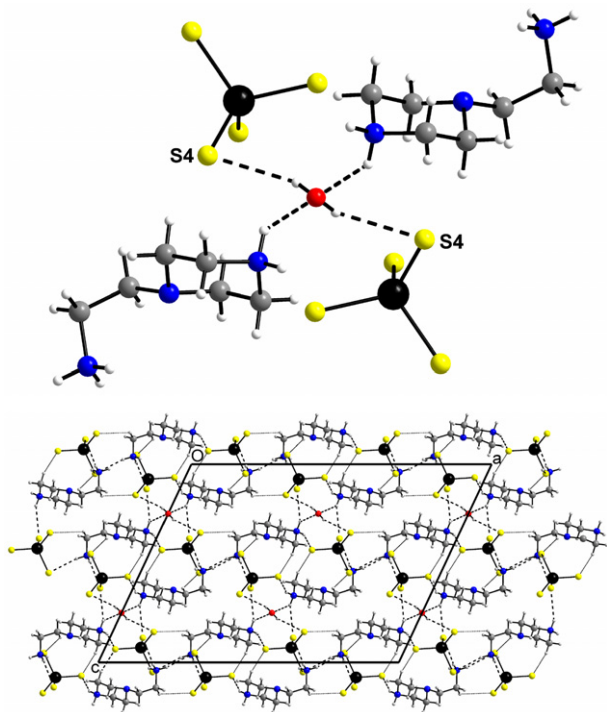


Fig. 4. Hydrogen bonding situation around the crystal water molecule in **3** showing the linking of two symmetry related cations and anions by the crystal water (top). A view of the extended H-bonded network in the crystallographic *ac*-plane, showing the formation of alternating layers (bottom). Hydrogen bonding is shown as dashed lines.

in their Raman spectrum at around 455 cm^{-1} , which can be assigned to the $\nu_1(A_1)$ vibration. The bands at around 200 and 190 cm^{-1} in the IR–Raman spectra of **1–4** can be assigned to the ν_4 .

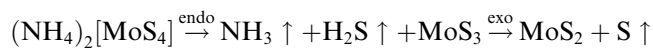
3.4. Comparative structural chemistry of tetrathiomolybdates

In addition to the tetrathiomolybdates **1–3** reported herein, several others have been structurally characterized [10–16,38–48]. The isolation of $[\text{MoS}_4]^{2-}$ anions with a variety of cations like ammonium, K^+ , metal complex cations like $[\text{Co}_2(\text{tren})_3]^{2+}$, $[\text{Mn}(\text{dien})_2]^{2+}$, $[\text{Ni}(\text{en})_3]^{2+}$, several organic ammonium cations like $(\text{enH}_2)^{2+}$, $(N\text{-Me-enH}_2)^{2+}$, $(\text{dipnH}_2)^{2+}$, $(1,3\text{-pnH}_2)^{2+}$, $(1,4\text{-bnH}_2)^{2+}$, $(\text{trenH}_2)^{2+}$, $(\text{pipH}_2)^{2+}$ (for the explanation of abbreviations see Table 6) tetralkylammonium cations, etc. indicates the flexibility of the MoS_4 tetrahedron to exist in different structural environments. The structural parameters of 28 tetrathiomolybdates are listed in Table 6 of which $(\text{trenH}_2)[\text{MoS}_4] \cdot \text{H}_2\text{O}$ and $(2\text{-pipH-1-EtNH}_3)[\text{MoS}_4] \cdot 1/2\text{H}_2\text{O}$ (**3**) are the only known structurally characterised hydrates and both exhibit more varieties of H-bonding interactions. A comparison reveals that the ammonium, K^+ , Rb^+ , Cs^+ and methylammonium tetrathiomolybdates are isostructural and crystallise in the centrosymmetric *Pnma* space group while three of the four known $[\text{MoS}_4]^{2-}$ compounds with metal complex cations crystallise in non-centrosym-

metric space groups. The use of chiral amines like $[\text{PhCH}(\text{CH}_3)\text{NH}_2]$ results in tetrathiomolybdates crystallising in chiral space groups [15]. Interestingly the use of tetralkylammonium cations like $(\text{NR}_4)^+$ ($\text{R} = \text{methyl or butyl}$) results in non-centrosymmetric solids. It is to be noted that for the $(\text{NEt}_4)^+$ salt of $[\text{MoS}_4]^{2-}$ in addition to the reported triclinic $P\bar{1}$ form, a polymorphic $P2_12_12_1$ has been identified [41]. As observed recently for $[\text{WS}_4]^{2-}$ compounds, the $[\text{MoS}_4]^{2-}$ compounds derived from *en*, *N-Me-en* and *dipn* crystallise in non-centrosymmetric groups [22,23]. In all compounds the MoS_4 tetrahedron is slightly distorted (Table 6), which can be attributed to the cation–anion interactions. In an earlier report we had shown that the Δ value in tetrathiotungstates can be taken as a useful measure of the distortion of the WS_4 tetrahedron and a threshold value of 0.03 was estimated. A very high Δ value of 0.1541 \AA was observed for $[\text{Co}(\text{dien})_2][\text{MoS}_4][\text{MoOS}_3]$ [42], where one of the S atoms is disordered and its position partially occupied by O resulting in a structure consisting of superimposed $[\text{MoS}_4]^{2-}$ and $[\text{MoOS}_3]^{2-}$ ions, being responsible for the unusually short Mo–S bond length. When the analysis is done keeping aside such compounds, it is observed that $(\text{pipH}_2)[\text{MoS}_4]$ [11] shows the longest Mo–S distance of 2.2114 \AA as well as the maximum Δ value of 0.0431 \AA , in analogy to the corresponding W compound. The average value of the Mo–S distance ranges from 2.1765 \AA in $[\text{Mn}(\text{dien})_2][\text{MoS}_4]$ [39] to 2.1921 \AA in $[(n\text{-Bu})_4\text{N}]_2[\text{MoS}_4]$ [34]. In general the average Mo–S bond distance for all compounds scatters in a small range and the Δ value is around 0.02 \AA . The Δ value for compound **1** is 0.0379 indicative of a distortion of the tetrahedron as evidenced by a comparison of the IR spectral bands in the Mo–S region (Fig. 5). In this analysis, a noticeable difference as compared to tetrathiotungstates is that more examples of non-centrosymmetric $[\text{MoS}_4]^{2-}$ compounds are observed.

3.5. Thermal investigations

It is well documented that ammonium tetrathiomolybdate undergoes a two-step decomposition to form MoS_2 [2,49] as shown below:



In contrast, organic ammonium tetrathiomolybdates decompose endothermically in a single step in most cases [11,12] and the final amorphous residue always contains considerable amounts of C [50]. In a recent report we have shown that tetralkylammonium tetrathiomolybdates exhibit a complex thermal behaviour involving structural phase transitions as well as emissions of different organic fragments like disulfides and amines [50]. For the decomposition of **1–4** (argon atmosphere; heating rate of 4 K) no exothermic events were observed. Although the exact nature of the intermediates formed cannot be described in the absence of mass spectral data of the emitted fragments,

Table 6
Comparative structural parameters of tetrathiomolybdates

Compound	Space group	Mo–S long (Å)	Mo–S short (Å)	Difference Δ (Å)	Mo–S mean (Å)	Ref.
(NH ₄) ₂ [MoS ₄]	<i>Pnma</i>	2.186	2.171	0.015	2.178	[43]
Rb ₂ [MoS ₄]	<i>Pnma</i>	2.1917	2.1782	0.0135	2.182	[38]
Cs ₂ [MoS ₄]	<i>Pnma</i>	2.1935	2.1809	0.0126	2.1841	[45]
K ₂ [MoS ₄]	<i>Pnma</i>	2.2000	2.1757	0.0243	2.1823	[46]
(MeNH ₃) ₂ [MoS ₄]	<i>Pnma</i>	2.1961	2.1762	0.0199	2.1841	[16]
[Co(dien) ₂] ₂ [MoS ₄][MoOS ₃] [*]	<i>P2₁/n</i>	2.2041	2.050	0.1541	2.1568	[42]
(tmenH ₂)[MoS ₄]	<i>P2₁/n</i>	2.1983	2.1694	0.0289	2.1838	[12]
(1,3-pnH ₂)[MoS ₄]	<i>P2₁/c</i>	2.1882	2.1699	0.0183	2.1815	[12]
(trenH ₂)[MoS ₄] · H ₂ O	<i>P2₁/c</i>	2.1951	2.1670	0.0281	2.1846	[11]
(pipH ₂)[MoS ₄]	<i>P2₁/c</i>	2.2114	2.1683	0.0431	2.1872	[11]
(1,4-bnH ₂)[MoS ₄]	<i>P1̄</i>	2.1992	2.1749	0.0243	2.1814	[13]
(<i>trans</i> -1,4-cnH ₂)[MoS ₄]	<i>P1̄</i>	2.1955	2.1774	0.0181	2.1865	[14]
[(Et) ₄ N] ₂ [MoS ₄] [†]	<i>P1̄</i>	2.187	2.171	0.016	2.179	[44]
(<i>trans</i> -1,2-cnH ₂)[MoS ₄]	<i>C2/c</i>	2.1876	2.1751	0.0125	2.1814	[14]
[(<i>n</i> -Pr) ₄ N] ₂ [MoS ₄]	<i>C2/c</i>	2.1928	2.1749	0.0179	2.1850	[11]
(2-pipH-1-EtNH ₃)[MoS ₄] · 1/2H ₂ O (3)	<i>C2/c</i>	2.2005	2.1703	0.0302	2.1835	this work
[Co ₂ (tren) ₃][MoS ₄]	<i>Fdd2</i>	2.1901	2.1631	0.0270	2.180	[39]
[Ni(en) ₃][MoS ₄]	<i>Pna2₁</i>	2.1865	2.1766	0.0099	2.1817	[34]
[Mn(dien) ₂][MoS ₄]	<i>I-4</i>	2.1765	2.1765	0.0	2.1765	[40]
[(Me) ₄ N] ₂ [MoS ₄] [#]	<i>P2₁2₁2₁</i>	2.177	2.159	0.018	2.171	[41]
[(<i>n</i> -Bu) ₄ N] ₂ [MoS ₄]	<i>Fdd2</i>	2.2047	2.1792	0.0255	2.1921	[41]
(trienH ₂)[MoS ₄] [‡]	<i>Pca2₁</i>	2.200	2.173	0.027	2.185	[47]
(dabcoH)(NH ₄)[MoS ₄]	<i>P2₁3</i>	2.1854	2.1762	0.0092	2.1831	[48]
(enH ₂)[MoS ₄]	<i>P2₁2₁2₁</i>	2.1846	2.1735	0.0111	2.179	[10]
<i>R</i> -[PhCH(CH ₃)NH ₃] ₂ [MoS ₄]	<i>P2₁</i>	2.2066	2.1644	0.0422	2.1840	[15]
<i>S</i> -[PhCH(CH ₃)NH ₃] ₂ [MoS ₄]	<i>P2₁</i>	2.2056	2.1655	0.0401	2.1831	[15]
(<i>N</i> -Me-enH ₂)[MoS ₄] (1)	<i>P2₁2₁2₁</i>	2.2014	2.1635	0.0379	2.1861	this work
(dipnH ₂)[MoS ₄] (2)	<i>Pca2₁</i>	2.1903	2.1717	0.0186	2.1818	this work

Abbreviations used: MeNH₂ = methylamine; dien = bis(2-aminopropylamine); tmen = *N,N,N',N'*-tetramethylethylenediamine; 1,3-pn = 1,3-propanediamine; tren = tris(2-aminoethyl)amine; pip = piperazine; 1,4-bn = butane-1,4-diamine; *trans*-1,4-cn = *trans*-1,4-diaminocyclohexane; Et = ethyl; *trans*-1,2-cn = *trans*-1,2-diaminocyclohexane; *n*-Pr = *n*-propyl; en = ethylenediamine; Me = methyl; *n*-Bu = *n*-butyl; trien = triethylenetetramine; dabco = 1,4-diazabicyclo-2,2,2-octane; [PhCH(CH₃)NH₂] = α -methylbenzylamine. ^{*}One S atom is disordered. [†]Two crystallographically independent [MoS₄]²⁻ units; [#]three crystallographically independent [MoS₄]²⁻ units. The cations are disordered; for compounds with more than one independent [MoS₄]²⁻ units the parameters are listed for that unit which shows maximum Δ .

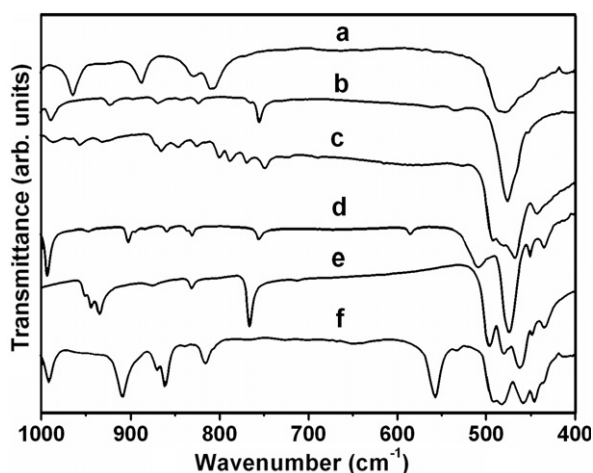


Fig. 5. IR spectra of (a) (enH₂)[MoS₄], (b) (dipnH₂)[MoS₄], (c) (dienH₂)[MoS₄], (d) (2-pipH-1-EtNH₃)[MoS₄] · 1/2H₂O, (e) (*N*-Me-enH₂)[MoS₄], (f) (pipH₂)[MoS₄] showing asymmetric stretching vibration (ν_3).

it is interesting to note that the thermal patterns exhibit a common trend. The decomposition temperatures and the composition of the final sulfide residues are collected in

Table 7. The composition of the residues is in good agreement with that derived from EDX analysis. The X-ray powder patterns of the final C and N containing molybdenum sulfide residues of **1–4** showed only broad humps indicating their amorphous nature.

Compound **1** exhibits two endothermic events at 124 and 153 °C, assignable to the decomposition of the organic cation as well as tetrathiomolybdate. The total mass loss up to 600 °C is 37.6%. The elemental analysis of the final product showed the presence of C and N and can be formulated as MoS_{2.3}C_{1.3}N_{0.4}. For **2** the endothermic signal at 73 °C can be attributed to a phase transition and a similar behaviour was observed recently for tetralkylammonium thiomolybdates [50]. Compound **2** is thermally stable up to 116 °C and its decomposition is evidenced by the two endothermic events at 136 and 194 °C. The total mass loss up to 600 °C is 50.5% and is higher than expected for the loss of dipn and H₂S only (46.3%). The analysis of the residue is indicative of incomplete removal of organics.

In the TG-DTA curve of **3** (Fig. 6), the first mass loss around 100 °C, is accompanied by an endothermic peak at 107 °C. The mass loss of 2.68% and is in very good agreement for the loss of half mole of water (expected is 2.47%). The anhydrous compound thus formed starts

Table 7
Thermal characterization data for 1–4

Complex	DTA temp (°C)	TG mass loss (%)	Elemental analysis of residue (%)	Final residue
(<i>N</i> -Me-enH ₂)[MoS ₄] (1)	124 endo 153 endo	37.60	C 8.15 H 0.25 N 3.19 S 37.97	MoS _{2.3} C _{1.3} N _{0.4}
(dipnH ₂)[MoS ₄] (2)	136 endo 183 endo	50.51	C 6.79 H 0.27 N 1.69 S 37.66	MoS _{2.1} C _{1.01} N _{0.2}
(2-pipH-1-EtNH ₃)[MoS ₄] · 1/2H ₂ O (3)	107 endo 160 endo	2.68 41.75	C 14.79 H 0.47 N 5.07 S 29.45	MoS _{1.7} C _{2.4} N _{0.7}
(dienH ₂)[MoS ₄] (4)	153 endo 187 endo	37.68	C 13.03 H 0.61 N 4.67 S 34.32	MoS _{2.2} C _{2.2} N _{0.7}

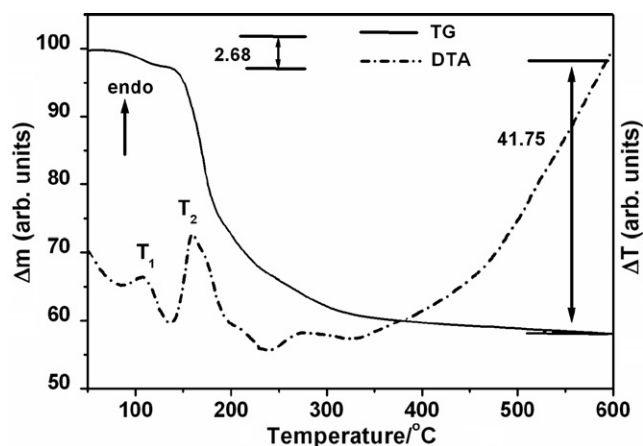


Fig. 6. TG and DTA curves for (2-pipH-1-EtNH₃)[MoS₄] · 1/2H₂O (3) (heating rate 4 K/min; Ar atmosphere; T₁ = 107 and T₂ = 160 °C are peak temperatures).

decomposing endothermically as evidenced by the signal at 160 °C and a sharp mass drop in the TG curve. A total mass loss of 44.43% up to 600 °C is quite less than expected for the removal of water, amine and H₂S (47.27%). Based on analytical data the residue can be formulated as MoS_{1.7}C_{2.3}N_{0.7}. The Mo:S ratio is 1:1.7 instead of 1:2 indicating the presence of some structural C. Compound 4, which exhibits two endothermic events at 153 and 187 °C, is stable up to about 130 °C and decomposes with a total mass loss of 37.68% up to 500 °C, which is lower than expected for the emission of dien and H₂S (41.66%). The elemental analysis of the residue indicates MoS_{2.2}C_{2.2}N_{0.7} as composition.

4. Conclusions

The organic ammonium tetrathiomolybdates 1–4 were synthesized by an aqueous reaction of (NH₄)₂[MoS₄] with the corresponding organic amines. All the compounds were

characterised by elemental analysis, spectroscopy methods, and the structures of 1–3 were determined. In compounds 2–4 the triamines are partially protonated forming dications. The characterization of such compounds demonstrates the ability of [MoS₄]²⁻ to stabilise partially protonated organic ammonium cations. A comparative study of structural data of several tetrathiomolybdates highlights, that in most of the compounds the average Mo–S bond length scatters in a relatively narrow range, i.e. this structural parameter cannot be regarded as a good measure of the actual distortion of the anions. A more sensitive parameter is the difference Δ between the longest and shortest Mo–S bonds. Above a critical value for Δ the symmetry of the MoS₄ tetrahedron is reduced which is reflected by the appearance of extra signals in the Mo–S region of the infrared spectrum. The compounds 1–4 decompose endothermically and the resulting decomposition products are amorphous carbon contaminated metal sulfides with compositions MoS_{2.3}C_{1.3}N_{0.4}, MoS_{2.1}C_{1.01}N_{0.2}, MoS_{1.7}C_{2.4}N_{0.7} and MoS_{2.2}C_{2.2}N_{0.7}, respectively.

Acknowledgements

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Appendix A. Supplementary material

CCDC 651723, 651724, 651725 contain the supplementary crystallographic data for 1, 2 and 3. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge

CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.08.023.

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