# Synthesis and X-ray structure characterization of ethylenediammonium tetrathiomolybdate

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The passage of hydrogen sulphide gas into an aqueous ammonium heptamolybdate solution in the presence of ethylenediamine leads to the formation of stable ethylenediammonium tetrathiomolybdate **1** in good yields. The title compound has been characterized by IR, UV-Vis and elemental analysis and its structure has been determined by single crystal X-ray crystallography. Ethylenediammonium tetrathiomolybdate crystallizes in the orthorhombic space group $P2_12_12_1$ with the following unit cell dimensions for $C_2H_{10}N_2S_4Mo$ (M=286.3) a=8.582(5) Å, b=9.276(5) Å, c=11.792(5) Å, $\alpha = \beta = \gamma = 90°$ v = 938.7(8) $Å^3$, Z=4, $D_c$=2.026 $g.cm^{-3}$. The structure of the title compound consists of tetrahedral tetrathiomolybdate anions, which form an extended three dimensional network in the solid state, with the aid of N-H---S as well as C-H---S hydrogen bonding interactions with the organic cation.

The chemistry of molybdenum with sulphur donor ligands is unique when compared to other transition metal ions[1]. The diversity in structural and reactivity characteristics of Mo/S complexes is an important reason for the continuing research in this rapidly growing field. Interest in sulphur containing compounds of Mo and W is also due to their implications in bioinorganic chemistry and industrial catalysis[2-4]. Sulphur-coordinated transition metals engage in facile electron and proton transfer processes which are important for active-site turnover in biosystems[5]. In industry, metal sulphides such as $MoS_2$ and $WS_2$ are central to hydrotreating catalysis including the removal of sulphur (hydrodesulphurization), nitrogen (hydrodenitrogenation), oxygen (hydrodeoxygenation) and metals (hydrodemetalation) from petroleum fractions. In view of their importance in existing systems and their potential use in future systems, a better understanding of metal sulphide complexes may prove valuable in the design of next-generation catalysts.

The ammonium salt of tetrathiomolybdate $(NH_4)_2MoS_4$ **2** has been routinely used as the starting material in synthetic Mo/S chemistry for the preparation of several compounds ranging from insoluble sulphides[6] like $MoS_3$ and $MoS_2$ to soluble sulphur rich binary and tertiary thiomolybdates as well as heterobimetallic complexes[1,7]. However, in all the syntheses it has been recommended to use either freshly pre-

pared (or stored under inert atmosphere) sample of the ammonium salt in view of its slow decomposition in air to $(Mo_2O_2S_6)^{2-}$ via an induced electron transfer reaction[8]. The tetrathiomolybdates can also function like bidentate ligands coordinating to a variety of transition metal ions forming sulphur bridged heterobimetallic complexes[7,9]. In recent years, the use of piperidinium[10] and benzyltriethylammonium[11] tetrathiometalates as reagents in organic syntheses, for the facile formation of several novel organic sulphur compounds has added an entire new dimension to this field. Although a few salts of tetrathiomolybdate other than the ammonium salt are known, there is a need to prepare other cationic tetrathiomolybdates in view of the rich synthetic chemistry associated with tetrathiomolybdate as mentioned above. Herein, we wish to report on the synthesis and single crystal structural characterization of the stable ethylenediammonium tetrathiomolybdate.

## Materials and Methods

Solvents and reagents were used as obtained from commercial sources in this investigation. Ammonium tetrathiomolybdate **2** was prepared by following a published procedure[12]. Infrared spectra were recorded on a Shimadzu DR-8031 FT-IR instrument. The samples were pressed as KBr pellets and referenced to polystyrene bands. UV-Vis spectra were recorded on a Shimadzu UV-1601 instrument using matched quartz cells. The X-ray structure determination was performed at the National Single Crystal X-ray facility

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at IIT Kanpur. C, H, N and S were analyzed at the Microanalytical Laboratories IIT Kanpur.

*Preparation of ethylenediammonium tetrathiomolybdate 1*

**Method 1**

A steady stream of hydrogen sulphide gas was passed through an aqueous solution of ammonium heptamolybdate (2g in 20 ml) containing 6 ml of 99% ethylenediamine. The reaction temperature was maintained at 60°C. After 30-40 min of gas passing, copious amounts of garnet red crystals slowly separated. The gas passing was stopped and the reaction mixture cooled in an ice-bath for ~15 min. The red crystals were filtered at the pump, washed with a few ml of ice-cold water followed by isopropanol and ether and dried *in vacuo*. Yield 2.8 g (~80%).

IR data : 3000 (br), 1570, 1540, 1460, 1440, 1325, 1305, 1080, 1030, 1010, 970, 885, 805, 474 cm$^{-1}$

UV-Vis data: 466, 316, 240 nm

Anal. Found (Calcd): C 8.36 (8.39), H 3.7 (3.50), N 9.98 (9.79), S 44.25 (44.75)%.

**Method 2**

Freshly prepared ammonium tetrathiomolybdate **2** (260 mg, 1 mmol) was dissolved in water (15 ml). To this solution ethylenediamine (1 ml) was added and the reaction mixture filtered and kept in the refrigerator for crystallization. After 3-4 days deep garnet red blocks of the title compound had formed. The crystals were isolated by filtration, washed with a small amount of water followed by isopropanol and ether and air dried. The product obtained (170 mg) in this method had an identical IR, UV-Vis and analysed satisfactorily as the product from Method 1. The crystals obtained in this method were suitable for X-ray studies.

**Results and Discussion**

*Synthesis*

The synthesis of the title compound can be readily accomplished in good yields by the exhaustive hydrogen sulphide treatment of an aqueous heptamolybdate solution in the presence of ethylenediamine. The replacement of oxo groups in the starting material by the sulphido groups in the title compound can be represented by the following Eq. (1).

$$(NH_4)_6(Mo_7O_{24}) + en(excess) \rightarrow (enH_2)(MoO_4) \xrightarrow{H_2S} 1 \quad ... (1)$$
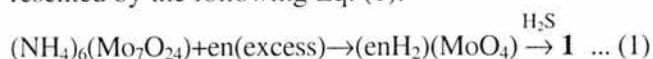
where en stands for ethylenediamine.

The first step in the synthesis is the formation of ethylenediammonium tetraoxomolybdate (enH$_2$)(MoO$_4$)

in the presence of excess ethylenediamine. This then undergoes ligand exchange on treatment with H$_2$S resulting in the formation of the product. The formation of **1** from the preformed **2** on treatment with ethylenediamine can be explained as a cation exchange reaction by the stronger base ethylenediamine as shown in Eq. (2). Our efforts to isolate the corresponding W analogue under identical conditions have not been fruitful.

$$(NH_4)_2MoS_4 + en (excess) \rightarrow 1 + 2 NH_3 \quad ... (2)$$
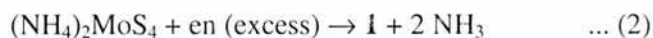
The product synthesized from both the above methods is extremely air stable and very less soluble in water unlike the ammonium salt. Ethylenediammonium tetrathiomolybdate **1** is soluble in DMF but insoluble in CH$_3$CN. It has been reported[8] that ammonium tetrathiomolybdate **2** slowly decomposes in air, via an induced electron transfer reaction resulting in the formation of the dinuclear $(Mo_2O_2S_6)^{2-}$ species and this process is quite facile under laboratory atmosphere. In contrast, **1** is extremely stable. The unusual stability of **1** compared to that of **2** can be attributed to the nature of the counter cation in the title complex. It may be noted that all previous known salts of $(MoS_4)^{2-}$ contain two monovalent cations which are either ammonium or cesium or tetraalkylammonium. It appears that the difference in stabilty is due to the dicationic nature of ethylenediammonium cations. Such a behaviour is not unprecedented, as it is well established that the charge on the cation is crucial for the stabilization of a particular anion. This is well demonstrated[13] by the isolation of pentacoordinate $[Ni(CN)_5]^{3-}$ trianionic complex as the salt of $[Cr(en)_3]^{3+}$. The extra stability of the title compound can be further attributed to the hydrogen bonding interactions of the tetrathiomolybdate anion and the ethylenediammonium cation via both N-H---S and C-H---S bonds resulting in the formation of a three dimensional network (vide infra) as established by X-ray analysis.

*Spectral studies*

A combination of IR, UV-Vis and elemental analysis techniques has been employed to characterize **1**. The solid state infrared spectrum of **1** exhibits a strong signal at 474 cm$^{-1}$ and this is assigned to the $\nu_{Mo=S (asymmetric)}$ vibration while all the other signals can be attributed to as originating from the organic ethylenediammonium counter cation. The triply degenerate Mo=S asymmetric stretching vibration occurs at a lower energy compared to that in the ammonium salt

Table 1 — Crystal data and structure refinement for $(enH_2)MoS_4$

| | |
|---|---|
| Identification code | $(enH_2)MoS_4$ |
| Molecular formula | $C_2H_{10}MoN_2S_4$ |
| Formula weight | 286.30 |
| Temperature | 293(2) K |
| Wavelength | 0.71069 Å |
| Crystal system, space group | orthorhombic, $P2_12_12_1$ |
| Unit cell dimensions | a = 8.582(5) Å alpha = 90.000 deg. |
| | B = 9.276(5) Å beta = 90.000 deg. |
| | c = 11.792(5) Å gamma = 90.000 deg. |
| Volume | 938.7(8) Å$^3$ |
| Z, Calculated density | 4, 2.026 g.cm$^{-3}$ |
| Absorption coefficient | 2.214 mm$^{-1}$ |
| F(000) | 568 |
| Crystal size. | $2 \times 2 \times 2$ mm |
| Theta range for data collection | 2.79 to 22.55 deg. |
| Limiting indices | $-9 <= h <= 0$, $-9 <= k <= 0$, $-12 <= P < 12$ |
| Reflections collected / unique | 1403 / 1226 [R(int) = 0.0688] |
| Completeness to theta = 22.55 | 99.5 % |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 1226 / 0 / 122 |
| Goodness-of-fit on F$^2$ | 0.786 |
| Final R indices [I>2sigma(I)] | R1 = 0.0293, wR2 = 0.0828 |
| R indices (all data) | R1 = 0.0304, wR2 = 0.0840 |
| Absolute structure parameter | 0.00(8) |
| Largest diff. peak and hole | 0.559 and -0.829 e.Å$^3$ |

Table 2 — Bond lengths [Å] and bond angles [deg] for **1**

| | |
|---|---|
| S(4)-Mo(1) | 2.1846(17) |
| S(2)-Mo(1) | 2.1735(18) |
| C(1)-N(1) | 1.474(11) |
| C(1)-C(2) | 1.493(10) |
| N(2)-C(2) | 1.478(10) |
| Mo(1)-S(3) | 2.1783(17) |
| Mo(1)-S(1) | 2.1792(19) |
| N(1)-C(1)-C(2) | 113.3(6) |
| S(2)-Mo(1)-S(3) | 109.41(7) |
| S(2)-Mo(1)-S(1) | 108.39(8) |
| S(3)-Mo(1)-S(1) | 109.51(7) |
| S(2)-Mo(1)-S(4) | 109.83(7) |
| S(3)-Mo(1)-S(4) | 109.49(7) |
| S(1)-Mo(1)-S(4) | 110.20(7) |
| N(2)-C(2)-C(1) | 113.2(6) |

Symmetry transformations used to generate equivalent atoms

$(\nu_{Mo=S\ (asymmetric)} = 480$ cm$^{-1}$). Such a shift has also been reported in the tetraethylammonium salt[12] which exhibits a signal at 470 cm$^{-1}$. This behaviour has been attributed to the change in cation. The electronic spectrum of **1** in $H_2O$ exhibits bands at 466, 316 and 240 nm. The peak positions observed in **1** are almost identical within experimental error to the corresponding ammonium or tetraethylammonium salts[12].

*X-ray crystallographic procedure*

Crystals suitable for the X-ray study were grown by the slow evaporation of an aqueous solution of **2** in the presence of excess ethylenediamine. A single crystal suitable for X-ray diffraction was chosen from this crop and mounted on an Enraf-Nonius CAD4 four-circle diffractometer for the cell determination and intensity data collection employing Mo-Kα radiation. Intensity data for the crystal were obtained with the use of a θ-2θ step scan technique. Lattice parameters were obtained by the least-square analysis of 25 machine centered reflections. The intensities of three standard reflections were monitored periodically (every 97 reflections) throughout the course of data collection and no significant decay was detected. Other details pertaining to data collection and refinement are listed in Table 1.

The data were reduced[14] and the structure was solved using the WinGX program[15] (Version 1.63) and incorporating SHELXL-97[16] for refinement by least-square methods based on F$^2$. The non hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in the model at their calculated positions. Selected interatomic parameters are collected in Table 2 and the crystallographic numbering scheme is shown in Fig. 1 which was drawn with ORTEP-III at 50% probability ellipsoids. The fractional atomic coordinates for non hydrogen atoms are collected in Table 3, while the anisotropic thermal parameters are tabulated in Table 4.

*Crystal structure of 1*

The thermal ellipsoid plot of **1** showing the immediate coordination environment around the central metal is shown in Fig. 1. The hydrogen atoms have been omitted from the structure for clarity. The compound crystallizes in the orthorhombic space group $P2_12_12_1$. The Mo(VI) ion is tetracoordinated and all the four sites are occupied by the sulphido ligands.

Table 3—Fractional Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for (enH$_2$)MoS$_4$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

|  | x | y | z | U(eq) |
|---|---|---|---|---|
| S(4) | 7534(2) | 2909(2) | -304(1) | 30(1) |
| S(2) | 5866(2) | 6103(2) | 861(2) | 29(1) |
| C(1) | 8152(9) | -760(8) | 1367(7) | 39(2) |
| N(2) | 5679(7) | 580(8) | 1641(6) | 31(1) |
| Mo(1) | 7717(1) | 4520(1) | 1040(1) | 19(1) |
| N(1) | 9304(8) | 419(9) | 1338(6) | 30(1) |
| S(1) | 9947(2) | 5636(2) | 932(2) | 30(1) |
| C(2) | 6800(8) | -459(8) | 2128(6) | 32(2) |
| S(3) | 7518(2) | 3467(2) | 2685(1) | 29(1) |

Table 4 — Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1** (enH$_2$)MoS$_4$

|  | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| S(4) | 33(1) | 29(1) | 27(1) | -6(1) | -3(1) | 0(1) |
| S(2) | 25(1) | 32(1) | 30(1) | -1(1) | -1(1) | 6(1) |
| C(1) | 29(4) | 30(4) | 56(5) | -10(3) | 6(4) | 1(3) |
| N(2) | 12(3) | 47(4) | 34(3) | 3(3) | 7(3) | 2(3) |
| Mo(1) | 15(1) | 23(1) | 20(1) | -1(1) | 0(1) | 0(1) |
| N(1) | 24(3) | 32(4) | 34(4) | 2(3) | 4(3) | 7(3) |
| S(1) | 21(1) | 42(1) | 28(1) | -3(1) | 2(1) | -7(1) |
| C(2) | 32(4) | 28(4) | 35(4) | 4(3) | 2(3) | -3(3) |
| S(3) | 30(1) | 34(1) | 22(1) | 5(1) | 0(1) | -1(1) |

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 hka^*b^* U_{12}]$
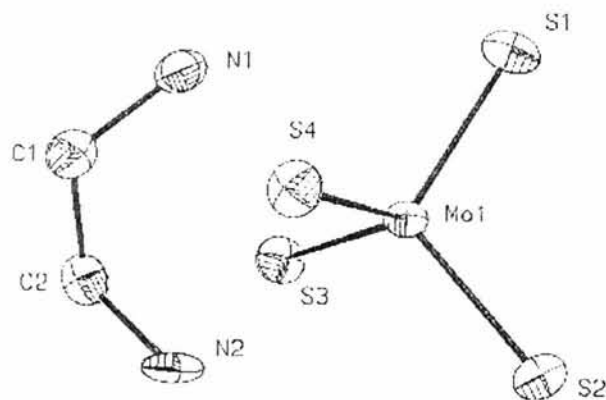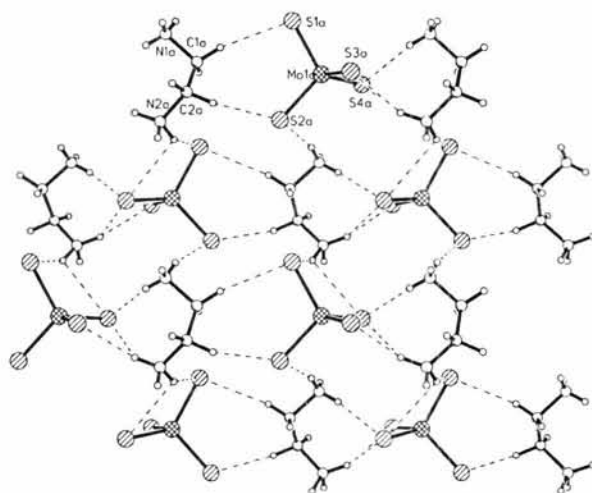


Fig 1—Molecular structure and crystallographic numbering scheme employed for **1** (C$_2$H$_{10}$N$_2$S$_4$Mo). H atoms are omitted for clarity.



Fig 2 — View of the two dimensional hydrogen bonded sheet of **1** viewed down the *c* axis.

The central metal is in a near tetrahedral environment and the S-Mo-S bond angles are very close to the tetrahedral values ranging from 108.39(8)° to 110.20(7)°. The metal sulphur bond lengths are nearly equal ranging from 2.1735(18)Å to 2.1846(17) Å. The crystal structures of the ammonium[17] and the tetraethyl-ammonium[18] tetrathiomolybdates are the only ones of the mononuclear, tetrathio type, reported in the literature, to our knowledge. The crystal structure of ammonium tetrathiomolybdate has been shown to be isomorphous with β-K$_2$SO$_4$. The average Mo-S bond length in the ammonium salt is 2.178 Å while it has been mentioned[7] that the deviations of the mean bond lengths in salts with other cations such as Cs$^+$ and (PPh$_4$)$^+$ cannot be significantly interpreted. The M-S bond length in **2** is intermediate between that of a Mo-S single bond and Mo=S double bond, indicative of the involvement of π–bonding. We propose a similar formulation for the title compound **1** based on the

above consideration. The C-C and C-N bond lengths and bond angles are typical of a saturated amine.

The detailed analysis of the structure indicates the existence of cation and anion interactions via hydrogen bonds. Interestingly, the sulfido ligands in the title compound indulge in two types of hydrogen bonding, both N-H---S and C-H---S bonding interactions with the organic cation resulting in the formation of an extended three dimensional-network in the solid state. Fig. 2 presents a view of the two-dimensional hydrogen bonded sheet of **1** viewed down the *c* axis. These hydrogen bonded sheets further link together resulting in the formation of an extended three dimensional polymeric network (Fig. 3). Although the presence of strong hydrogen bonds has been reported[7] in the ammonium salt of dioxodithiomolybdate, to our knowledge, there is no precedence
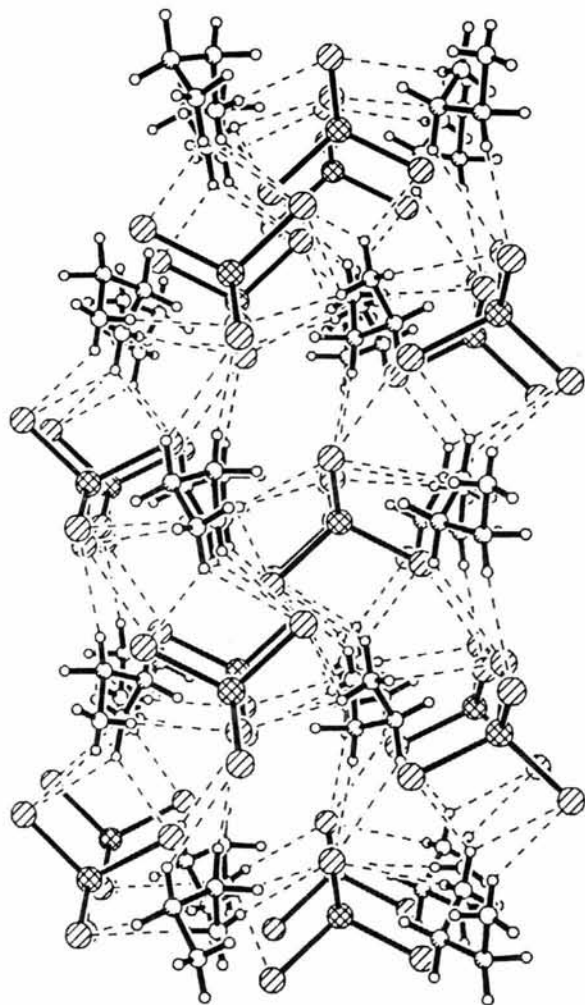
Fig 3 — View down the *a* axis showing the three dimensional hydrogen bonded network in **1**.

for such hydrogen bonding network in tetrathiomolybdate chemistry. However, the formation of such polymeric networks with the aid of O-H---O and N-H---O hydrogen bonding interactions has been recently reported[19]. These hydrogen-bonding interactions seem to be responsible for the extraordinary stability of the title compound. Overall, the structure of the title compound **1** can be described as consisting of tetrahedral tetrathiomolybdate anions, which are linked to the ethylenediammonium cations, with the aid of N-H---S as well as C-H---S hydrogen bonding interactions resulting in the formation of an extended network in the solid state.

*Supporting information available*

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, on request quoting the deposition number 158439 for **1**.

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