

## Does an all-sulphur analogue of heptamolybdate exist?

BIKSHANDARKOIL R SRINIVASAN

Department of Chemistry, Goa University PO, Goa 403 206, India  
e-mail: srini@unigoa.ac.in

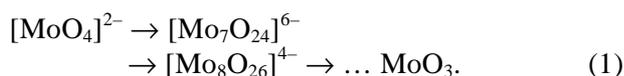
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**Abstract.** The complexes  $[\text{MoX}_4]^{2-}$  ( $\text{M} = \text{Mo}$ ;  $\text{X} = \text{O}$  or  $\text{S}$ ) exist as the monomeric tetrahedral species in aqueous alkaline solutions. Acidification of tetraoxomolybdate results in the condensation of the tetrahedral units via a series of polyoxomolybdates leading to the ultimate formation of the trioxide  $\text{MoO}_3$ . Heptamolybdate  $[\text{Mo}_7\text{O}_{24}]^{6-}$  is the first major polyanion of the acidification reaction. In contrast, acidification of tetrathiomolybdates leads to the formation of amorphous molybdenum trisulphide via a dinuclear  $\text{Mo(V)}$  complex. The formation of the dinuclear  $\text{Mo(V)}$  complex precludes the formation of any higher nuclearity  $\text{Mo(VI)-S}$  complexes in aqueous solution. Thus it is shown that the all-sulphur analogue of heptamolybdate  $[\text{Mo}_7\text{S}_{24}]^{6-}$  does not exist in alkaline medium and also cannot be isolated from aqueous acidic medium.

**Keywords.** Tetraoxomolybdate; heptamolybdate; tetrathiomolybdate; dinuclear; all-sulphur analogue.

### 1. Introduction

Group VI metals  $\text{Mo}$  and  $\text{W}$  exhibit a wide variety of stereochemistries as well as a variety of oxidation states. Their chemistry has been described as the most complex of those of the transition elements by Cotton.<sup>1</sup> The emerging chemistry of polyoxometalates<sup>2</sup> which exhibit fascinating structures like giant wheels,<sup>3,4</sup> giant wheels linked to chains,<sup>5</sup> giant molecular spheres of the Keplerate type,<sup>6,7</sup> giant molecular baskets<sup>8</sup> etc. is a testimony to the complex chemistry of  $\text{Mo}$ . In recent years, several polyoxomolybdates have been structurally characterised, representative examples being  $\text{Na}_7[\text{Mo}_7\text{O}_{24}]\text{OH} \cdot 21\text{H}_2\text{O}$ ,<sup>9</sup>  $(\text{dapH}_2)_2[\text{Mo}_8\text{O}_{26}]^{10}$  ( $\text{dapH}_2 = 1,3\text{-propanediammonium}$ ),  $(\text{dienH}_3)_2[\text{Mo}_9\text{O}_{30}]^{10}$  ( $\text{dienH}_3 = \text{diethylenetriammonium}$ ),  $\text{K}_8[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}]^{11}$  and  $[\text{La}(\text{H}_2\text{O})_7\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 4\text{H}_2\text{O}$ .<sup>12</sup> Interestingly all these complexes have been isolated from acidic media. The formation of the different oxomolybdates is pH dependent and can be summarised as below,



Acidification  $\longrightarrow$

Acidification of an aqueous alkaline solution of  $[\text{MoO}_4]^{2-}$  results in the condensation of the tetrahedral

$\text{MoO}_4$  units giving rise to polynuclear oxomolybdates. The ultimate product of the acidification is  $\text{MoO}_3$ , while the first product of the acidification reaction, at a pH below about 6, is the heptamolybdate<sup>13</sup>  $[\text{Mo}_7\text{O}_{24}]^{6-}$  which is made up of exclusively  $\text{MoO}_6$  octahedra in which all the metals retain the +6 state. The heptamolybdate has been shown to be the predominant intermediate<sup>14</sup> and has been isolated with a variety of cations from acidic media. From a structural point of view  $[\text{Mo}_7\text{O}_{24}]^{6-}$  is very interesting in view of its flexibility to exist in different structural environments, with different counter cations.<sup>15–22</sup> Anions with 8 and 36  $\text{Mo}$  atoms are also formed before the increasing acidity suffices to precipitate the hydrous oxide. Conversely, when  $\text{MoO}_3$  is dissolved in aqueous alkali or an organic amine, the resulting solution contains tetrahedral  $[\text{MoO}_4]^{2-}$  ions and simple or normal molybdates can be crystallized from this solution.<sup>23,24</sup>

$\text{Mo-S}$  compounds behave like the oxometalates, but with minor differences. Thus the tetrahedral ammonium tetrathiomolybdate  $(\text{NH}_4)_2[\text{MoS}_4]$  **1** complex is prepared<sup>25</sup> by reacting an ammoniacal solution of heptamolybdate with  $\text{H}_2\text{S}$ , a reaction first investigated by Berzelius.<sup>26</sup> In addition to its routine use as a starting material for the synthesis of a variety of polythiomolybdates<sup>27,28</sup> and S-bridged multimetallic complexes,<sup>29–32</sup> complex **1** has been shown to be a useful precursor for the preparation of amor-

phous  $\text{MoS}_3$ <sup>33</sup> and  $\text{MoS}_2$  nanotubes.<sup>34</sup> Further **1** has been introduced as a useful S-transfer reagent for the facile synthesis of organic disulphides in aqueous media.<sup>35</sup> The related complex benzyltriethylammonium tetrathiomolybdate  $[(\text{PhCH}_2)\text{N}(\text{C}_2\text{H}_5)_3]_2[\text{MoS}_4]$  that is soluble in organic solvents has been shown to be a versatile S-transfer reagent for the convenient synthesis of a variety of organo-sulphur compounds.<sup>36,37</sup> Acidification of  $[\text{MoS}_4]^{2-}$  results in the formation of the insoluble  $\text{MoS}_3$  as the ultimate product.<sup>33,38</sup>

Unlike the oxomolybdates, several of which can be isolated from acidic media, only two Mo–S complexes made up of the dinuclear  $\{\text{Mo}_2(\mathbf{m}\text{-S})_2(\text{X})_2\}^{2+}$  ( $\text{X} = \text{O}$  or  $\text{S}$ ) moiety, in which both Mo are reduced to +5, have been isolated till date by the acidification of aqueous tetrathiomolybdate.<sup>39,40</sup> The acidification reactions are further complicated in view of the induced electron-transfer reactions across the Mo–S bond which is a characteristic feature of Mo–S chemistry.<sup>41–43</sup> Like the heptamolybdate, it is likely that the hitherto unknown all-sulphur analogue of heptamolybdate can be an important link in the chain of events leading to the formation of  $\text{MoS}_3$ . In this context, the reported synthesis of  $(\text{NH}_4)_6[\text{Mo}_7\text{S}_{24}]$  **2**<sup>44</sup> and the corresponding organic ammonium complex  $[(\text{PhCH}_2)\text{N}(\text{C}_2\text{H}_5)_3]_2[\text{Mo}_7\text{S}_{24}]$  attracted our attention. The unusual aspect of this report is the isolation of the heptanuclear  $[\text{Mo}_7\text{S}_{24}]^{6-}$  complex from an alkaline medium under the Berzelius conditions. Hence we reinvestigated the earlier work by Kaushik and co-workers and reported<sup>45</sup> that the complex  $[(\text{PhCH}_2)\text{N}(\text{C}_2\text{H}_5)_3]_2[\text{Mo}_7\text{S}_{24}]$  is actually the well-documented S-transfer reagent  $[(\text{PhCH}_2)\text{N}(\text{C}_2\text{H}_5)_3]_2[\text{MoS}_4]$ . The present report is focused on the synthesis of the elusive  $[\text{Mo}_7\text{S}_{24}]^{6-}$  complex as the corresponding oxo analogue can be easily synthesized. The results of these investigations are described in this paper.

## 2. Experimental

All the chemicals used in this study were of reagent grade and used as received. Doubly distilled water was used as the solvent. The complexes  $(n\text{-Bu}_4\text{N})_2[\text{Mo}_2\text{OS}_7]$ <sup>39</sup> ( $n\text{-Bu} = n\text{-butyl}$ ) and  $[\text{Ni}(\text{en})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ <sup>46</sup> were prepared by literature methods. IR spectra were recorded on a Shimadzu (model 8101A) FTIR spectrometer in the range  $4000\text{--}400\text{ cm}^{-1}$ . The samples for the infrared spectra were prepared as KBr diluted pellets in the solid state and the infrared signals were referenced to polystyrene bands. Electronic

spectra were recorded in dilute ammonia using matched quartz cells on a Perkin–Elmer (Lambda 12) spectrophotometer. The pH measurements were made on a LabIndia pH meter. The ammonium content of compounds **1** and **2** were estimated as the insoluble ammonium tetraphenylborate.<sup>47</sup>

### 2.1 Preparation of $(\text{NH}_4)_2[\text{MoS}_4]$ **1**<sup>25</sup>

Ammonium heptamolybdate (3 g) was dissolved in water (5 ml). Liquor ammonia (13.5 ml, sp. gr. 0.91) was added to obtain a clear solution (pH = 12.1). Into this solution,  $\text{H}_2\text{S}$  gas was passed and the temperature was maintained at  $60^\circ\text{C}$  throughout the reaction. After 30 min when crystals started appearing, gas passage was stopped. The pH of the reaction mixture at this stage was found to be 10.51. The reaction mixture was cooled at  $0^\circ\text{C}$ . The crystals were isolated by filtration, washed well with isopropanol, followed by ether and dried *in vacuo*. Yield 4.1 g.

Anal. Found (Calcd) for  $(\text{NH}_4)_2[\text{MoS}_4]$ :  $(\text{NH}_4)$  13.85 (13.87), Mo 36.70 (36.85) S 49.11 (49.28)%. IR: ( $\nu_{(\text{Mo-S})}$ )  $478\text{ cm}^{-1}$ . UV-Vis (dil.  $\text{NH}_4\text{OH}$ ): 469, 317 and 242 nm.

### 2.2 Preparation of compound **2**<sup>44</sup>

Ammonium heptamolybdate (3 g) was dissolved in water (5 ml) and liquor ammonia (13.5 ml, sp. gr. 0.91) was added to obtain a clear solution (pH = 12.1). Into this solution  $\text{H}_2\text{S}$  gas was continuously passed for 5 h and the temperature was maintained at  $60^\circ\text{C}$  throughout the reaction. The pH of the reaction mixture at this stage was found to be 10.09. After 5 h of gas passing, the reaction mixture was cooled to  $0^\circ\text{C}$ . The solid was isolated by filtration, washed well with isopropanol, followed by ether and dried *in vacuo*. Yield 4.3 g. It is to be noted that after half an hour crystals of  $(\text{NH}_4)_2[\text{MoS}_4]$  started appearing in the solution. These crystals tend to block the passage of  $\text{H}_2\text{S}$  gas. Hence it is desirable to use a wide-mouthed gas-passing tube or alternatively change the tube periodically.

Anal. Found (Calcd) for  $(\text{NH}_4)_6[\text{Mo}_7\text{S}_{24}]$ :  $(\text{NH}_4)$  13.84 (6.98), Mo 36.70 (43.34) S 49.08 (49.68)%. IR: ( $\nu_{(\text{Mo-S})}$ )  $478\text{ cm}^{-1}$ ; UV-Vis (dil.  $\text{NH}_4\text{OH}$ ): 469, 317 and 242 nm.

*Note:* The analytical data are not in agreement with the proposed formula  $(\text{NH}_4)_6[\text{Mo}_7\text{S}_{24}]$  in ref. 44 but to  $(\text{NH}_4)_2[\text{MoS}_4]$  **1**.

### 2.3 Reactions of **1** and **2** with sodium tetraphenylborate

(NH<sub>4</sub>)<sub>2</sub>[MoS<sub>4</sub>] **1** (130 mg) was dissolved in water (10 ml). A solution of (360 mg) of sodium tetraphenylborate (NaBPh<sub>4</sub>) in water (30 ml) was slowly added in drops into the solution of **1** under stirring. This resulted in the immediate precipitation of NH<sub>4</sub>(BPh<sub>4</sub>). The reaction mixture was kept aside for 1 h and filtered. The white precipitate of NH<sub>4</sub>(BPh<sub>4</sub>) was washed well with ice-cold water till the washings were colourless, and then dried in vacuum and weighed to get 340.5 mg of precipitate. %NH<sub>4</sub> in **1** 13.85%. In another experiment, the reaction of 130 mg of compound **2** with (360 mg) of [NaBPh<sub>4</sub>] in water (30 ml) under identical conditions as mentioned above resulted in the formation of 336.3 mg of NH<sub>4</sub>(BPh<sub>4</sub>). %NH<sub>4</sub> in **2** 13.84%.

### 2.4 Reactions of **1** and **2** with [Ni(en)<sub>3</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O

A solution of (NH<sub>4</sub>)<sub>2</sub>[MoS<sub>4</sub>] **1** (260 mg) in water (15 ml) was added in drops into an aqueous solution of [Ni(en)<sub>3</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O (370 mg in 20 ml) under stirring. This resulted in the immediate precipitation of [Ni(en)<sub>3</sub>][MoS<sub>4</sub>]. The reaction mixture was kept aside for 1 h and filtered. The orange-red precipitate of [Ni(en)<sub>3</sub>][MoS<sub>4</sub>] was washed well with ice-cold water till the washings were colourless, and then dried in vacuum and weighed to get 460 mg of precipitate. %MoS<sub>4</sub> is 85.38. The use of 260 mg of **2** instead of **1** under identical conditions as mentioned above resulted in the formation of 461 mg of the orange precipitate of [Ni(en)<sub>3</sub>][MoS<sub>4</sub>]. %MoS<sub>4</sub> is 85.84.

### 2.5 Reaction of **1** with dilute HCl

(NH<sub>4</sub>)<sub>2</sub>[MoS<sub>4</sub>] **1** (650 mg) was dissolved in water (15 ml) and the pH of the red solution was found to be 7.99. Into this solution 0.6 ml of 2N HCl was added under continuous stirring. The colour of the solution changed to dark red and the pH of the solution at this stage had decreased to 7.11. Addition of [(*n*-Bu)<sub>4</sub>N]Cl (*n*-Bu = butyl) at this stage, afforded the dinuclear compound [(*n*-Bu)<sub>4</sub>N]<sub>2</sub>[Mo<sub>2</sub>OS<sub>7</sub>] as reported previously.<sup>39</sup> If no organic cation is added and acidification is continued, this results in the formation of an insoluble black compound MoS<sub>3</sub> below pH = 4.

### 2.6 Direct reaction of [Mo<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> with H<sub>2</sub>S

Ammonium heptamolybdate (1 g) was dissolved in water (20 ml) and a rapid stream of H<sub>2</sub>S gas was passed into this solution for 30 min. The colour of the solution changed from colourless to dark red at the end of 30 min. The dark red reaction mixture was left aside for crystallization. The electronic spectrum of the final reaction mixture was characteristic of complexes with a {Mo<sub>2</sub>(*m*-S)<sub>2</sub>}<sup>6+</sup> core<sup>39</sup> indicating the reduction of Mo(VI) to Mo(V). An aqueous solution of (*n*-Bu<sub>4</sub>N)Br (2 g in 10 ml) was added into the reaction mixture under stirring, resulting in the formation of a dark red complex. Filtration of the reaction mixture followed by washing with 2-propanol and ether yielded 2.1 g of the binuclear Mo(V) complex. The IR spectrum of the product with bands at 936 (*n*<sub>(Mo-O)</sub>), 516 (*n*<sub>(S-S)</sub>) and 469 (*n*<sub>(Mo-S)</sub>) cm<sup>-1</sup> matches well with that of the reported complex (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Mo<sub>2</sub>OS<sub>7</sub>].<sup>39</sup> In the absence of an added cation, no product could be isolated.

## 3. Results and discussion

### 3.1 Relevance of medium pH for synthesis

The pH values of aqueous solutions of the group VI tetraoxometalates and tetrathiometalates as well as that of heptamolybdate were determined and are collected in table 1. The saturated solutions of all the tetraoxometalates are quite alkaline as evidenced by their pH, excepting that of heptamolybdate which is acidic. When an excess aqueous ammonia is added to an acidic heptamolybdate solution the resulting pH (12.1) is more alkaline than that of saturated mo-

**Table 1.** pH values of some aqueous oxo and thiometalate solutions.

Compound	pH		
	0.01 M	0.1 M	Saturated
K <sub>2</sub> CrO <sub>4</sub>	8.81	9.74	10.58
Na <sub>2</sub> MoO <sub>4</sub>	6.97	8.59	9.69
Na <sub>2</sub> WO <sub>4</sub>	7.34	9.83	10.26
(NH <sub>4</sub> ) <sub>2</sub> [MoS <sub>4</sub> ] <b>1</b>	7.81	8.0	8.95
Compound <b>2</b>	7.83*	8.0	8.90
(NH <sub>4</sub> ) <sub>2</sub> [WS <sub>4</sub> ]	6.65	7.08	7.50
(NH <sub>4</sub> ) <sub>6</sub> [Mo <sub>7</sub> O <sub>24</sub> ]	5.18	—	5.3

\*This solution was prepared using 0.260 g of **2** in 100 ml

lybdate. Under this condition, only the tetrahedral  $[\text{MoO}_4]^{2-}$  species can exist in solution.<sup>1,24</sup> After  $\text{H}_2\text{S}$  gas is passed into this solution for 30 min the pH (10.51) of the solution is slightly decreased but the solution is still more alkaline than that of saturated tetrathiomolybdate. The decrease in pH can be attributed to the formation of thiomolybdate and also to the presence of  $\text{H}_2\text{S}$ , which is a weak acid in the reaction mixture. Cooling the reaction mixture and filtering affords ammonium tetrathiomolybdate **1** in high yields. The formation of  $(\text{NH}_4)_2[\text{MoS}_4]$  under these conditions is well known from the days of Berzelius and is well documented in the literature.<sup>25</sup> The reported synthesis of  $[\text{Mo}_7\text{S}_{24}]^{6-}$  essentially uses a similar reaction protocol.<sup>44</sup> However,  $\text{H}_2\text{S}$  gas is passed into the ammoniacal heptamolybdate solution (pH = 12.1) for an extended period of 5 h instead of 30 min for **1**. The pH of the reaction mixture after passing  $\text{H}_2\text{S}$  for 5 h was found to be 10.09 which is slightly less than that observed (10.51) for the synthesis of **1**. This can be easily explained as in this case the reaction mixture is quite saturated with  $\text{H}_2\text{S}$  in view of the long reaction time. However, the final reaction mixture is still alkaline and in fact more alkaline than that of the saturated solution of **1**. The pH data give the initial proof that the reaction mixtures in both cases are nearly identical and should give rise to the same products as further evidenced by analytical and spectral data (vide infra). For the formation of a heptanuclear Mo–S compound it is essential that S atoms are removed from the tetrahedral  $[\text{MoS}_4]^{2-}$  moiety in the form of  $\text{H}_2\text{S}$  as is done for heptamolybdate wherein the condensation of  $[\text{MoO}_4]^{2-}$  units are effected on acidification, by removing O in the form of  $\text{H}_2\text{O}$ . As the medium is strongly alkaline no such condensation can be effected. The reaction of compounds **1** and **2** with benzyltriethylammonium chloride results in cation exchange and the corresponding water insoluble but organic soluble organic ammonium thiomolybdates can be obtained. The role of the bulky organic cation is essentially to enhance the solubility in organic solvents.

### 3.2 Analytical and spectral studies

The mononuclear Mo–S compound **1** and the heptanuclear compound **2** can be readily distinguished in terms of the analytical data especially the % $\text{NH}_4$ . The ammonium content of both **1** and **2** were estimated gravimetrically as ammonium tetraphenylbo-

rate by using the same amount of **1** or **2** for analysis under identical conditions. The ammonium content of **2** (13.84) corresponds to  $(\text{NH}_4)_2[\text{MoS}_4]$  **1** (expected 13.87%) and not to a heptanuclear formulation **2** which requires an ammonium percentage of 6.98. This observation clearly indicates that not only are compounds **1** and **2** the same but also not even a trace of heptanuclear complex is formed under the reaction conditions. The identical nature of **1** and **2** can be further shown by the analysis of their thiomolybdate content as  $[\text{Ni}(\text{en})_3][\text{MoS}_4]$ . In a recent paper, it has been reported that the insoluble complex  $[\text{Ni}(\text{en})_3][\text{MoS}_4]$  can be obtained in excellent yields even under solvothermal conditions.<sup>48</sup> This suggested to us that the insoluble nature of the  $[\text{Ni}(\text{en})_3][\text{MoS}_4]$  complex can be used as a convenient method for determining the thiomolybdate content.<sup>49</sup> Thus the reaction of complex **1** or **2** with  $[\text{Ni}(\text{en})_3]^{2+}$  under aqueous conditions results in the formation of the highly insoluble complex  $[\text{Ni}(\text{en})_3][\text{MoS}_4]$  in quantitative yields. This reaction works equally well for water insoluble complexes like  $[(\text{PhCH}_2)\text{N}(\text{C}_2\text{H}_5)_3]_2[\text{MoS}_4]$ , indicating the generality of this method. In this case, the thiomolybdate is dissolved in  $\text{CH}_3\text{CN}$  and into this the Ni(II) complex is added resulting in the formation of  $[\text{Ni}(\text{en})_3][\text{MoS}_4]$ .<sup>49</sup> The infrared spectra of thiomolybdate complexes exhibit characteristic signatures for the Mo–S vibrations. The IR as well as the UV-Vis spectra of both the complexes are identical indicating that complexes **1** and **2** are one and the same. The triply degenerate asymmetric Mo–S stretching vibration is observed at  $478\text{ cm}^{-1}$  in both complexes and this value is in excellent agreement with the reported value for  $(\text{NH}_4)_2[\text{MoS}_4]$  **1**.<sup>25</sup> The UV-Vis spectra of **1** and **2** exhibit characteristic charge transfer bands of the  $[\text{MoS}_4]^{2-}$  moiety as reported.<sup>25,28</sup> The identical nature of both the spectra indicates that the chromophore present in **1** and **2** is one and the same. Based on the pH studies, analytical, and spectral data mentioned above, the formation of the heptanuclear  $[\text{Mo}_7\text{S}_{24}]^{6-}$  complex under alkaline conditions can be ruled out. It can be further stated that passing  $\text{H}_2\text{S}$  gas into an alkaline molybdate solution for an extended period does not result in the formation of any new Mo–S product other than the well known  $[\text{MoS}_4]^{2-}$ . This result is in accordance with the synthesis in alkaline media, as well as the structural characterization of several organic ammonium tetrathiomolybdate complexes.<sup>50–53</sup> The earlier reported<sup>44</sup> synthesis of  $(\text{NH}_4)_2[\text{Mo}_7\text{S}_{24}]$  is in effect a

cumbersome method for the preparation of  $(\text{NH}_4)_2[\text{MoS}_4]$ .

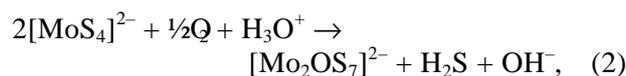
### 3.3 Comparative chemistry of heptamolybdate and its all-sulphur analogue

The above mentioned discussions clearly indicate that no heptanuclear Mo–S complex can be assembled in an alkaline medium. If the earlier reported complex is not the  $[\text{Mo}_7\text{S}_{24}]^{6-}$  complex, it is pertinent to know how such a complex can be synthesised at all. The comparative chemistry of polyoxo and polythio molybdates can be useful to derive a suitable answer to the problem of the synthesis of the elusive  $[\text{Mo}_7\text{S}_{24}]^{6-}$  complex. The known chemistry of oxomolybdates as well as thiomolybdates describes several polynuclear species. However, both the chemistries differ considerably. For example, complexes like  $[\text{Mo}_2\text{S}_{12}]^{2-}$ ,  $[\text{Mo}_3\text{S}_9]^{2-}$ ,  $[\text{Mo}_3\text{S}_{13}]^{2-}$  have no corresponding oxo analogues.<sup>27,28,54</sup> An important aspect of the Mo–S chemistry is the induced electron transfer across the Mo–S bond. Several polyoxomolybdates have been isolated from aqueous medium by acidification of the tetrahedral  $[\text{MoO}_4]^{2-}$ . In contrast, many of the known polythiomolybdates have been synthesised from non-aqueous media.

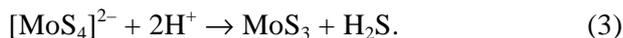
A primary requirement for the  $[\text{Mo}_7\text{S}_{24}]^{6-}$  complex is that all the Mo atoms be in +6 oxidation state. Further all the S ligands bound to Mo(VI) should be  $\text{S}^{2-}$  which can be either terminal or bridging to achieve charge balance. The presence of  $(\text{S}_2)^{2-}$  or  $(\text{S}_4)^{2-}$  type of ligands can be conveniently ruled out based on charge considerations. A survey of the known polynuclear thiomolybdates<sup>27,28</sup> indicates certain interesting features. Most of these complexes are synthesised under non-aqueous conditions. Most of the polythiometalates are anionic complexes isolated as organic salts by employing  $(\text{NEt}_4)^+$  or  $(\text{PPh}_4)^+$  counter cations, the only exceptions being the  $[\text{Mo}_2\text{S}_{12}]^{2-}$  and  $[\text{Mo}_3\text{S}_{13}]^{2-}$  complexes which are known as the ammonium salts. In almost all these complexes, at least one Mo is in a lower oxidation level namely +5 or even +4 as in  $[\text{Mo}_3\text{S}_{13}]^{2-}$ .<sup>53</sup> In addition to  $\text{S}^{2-}$ ,  $(\text{S}_2)^{2-}$  and  $(\text{S}_4)^{2-}$  type of ligands are also encountered in many of the polynuclear Mo–S complexes. The complexes  $[\text{Mo}_2\text{S}_{11}]^{2-}$  and  $[\text{Mo}_2\text{O}_2\text{S}_9]^{2-}$  are exceptions as in these dinuclear complexes both the Mo atoms retain their +6 state. A rational synthesis which employs  $(\text{PPh}_4)_2[\text{MoS}_4]$  in  $\text{CH}_3\text{CN}$ , S and acetic acid has been reported<sup>55</sup> for the synthesis of  $[\text{Mo}_2\text{S}_{11}]^{2-}$ . In view of the stability

of the tetrahedral  $[\text{MoS}_4]^{2-}$  core in alkaline media and the accessibility of dinuclear Mo–S complexes by acidification method, it appeared appropriate to investigate the acidification reactions of  $[\text{MoS}_4]^{2-}$  as a possible route for the synthesis of  $[\text{Mo}_7\text{S}_{24}]^{6-}$ . It is to be noted that heptamolybdate can be readily crystallized from an aqueous ammonium molybdate solution by acidification.<sup>15–22</sup> Further heptamolybdate exhibits the same structure in solution as in the solid state. Accordingly the reaction of aqueous  $[\text{MoS}_4]^{2-}$  was investigated with acid.

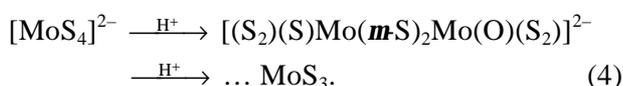
When an aqueous solution of  $(\text{NH}_4)_2[\text{MoS}_4]$  is acidified with HCl and the pH is reduced to around 7, colour change occurs accompanied by a change in the visible spectrum. At this stage, addition of tetrabutylammonium halide results in the formation of the known unsymmetrical dinuclear complex  $[\text{Mo}_2\text{OS}_7]^{2-}$  in which both the Mo atoms are reduced to +5. The formation of the dinuclear complex has been spectroscopically monitored by the visible spectrum and further confirmed based on the IR spectrum of the isolated compound. In the absence of an organic cation, no Mo–S complex can be isolated. Further acidification without adding any organic cation results in the formation of the insoluble black  $\text{MoS}_3$ , which exhibits a featureless infrared spectrum. All our efforts to isolate a trinuclear or polynuclear Mo–S complexes by the acidification of  $(\text{NH}_4)_2[\text{MoS}_4]$  were not fruitful. The only product in all these reactions was the amorphous  $\text{MoS}_3$ . It is pertinent to note that the reported yield of the dinuclear Mo(V) complex is about 60% and even in this case substantial amounts of  $\text{MoS}_3$  are obtained as by-product. The non-accessibility of polynuclear Mo–S complexes can then be attributed either to their hydrolytic instability or to the facile formation of  $\text{MoS}_3$  or both. It is interesting to note that controlled acidification using 0.5 moles of  $\text{H}^+$  per mole of  $[\text{MoS}_4]^{2-}$  leads to a predominantly dinuclear Mo(V) product while addition of two moles (excess) of acid results in the formation of the Mo(VI) complex  $\text{MoS}_3$ . The formation of the dinuclear complex has been represented by Pope<sup>39</sup> as follows:



wherein molecular  $\text{O}_2$  functions like an external oxidant to induce electron transfer across  $\text{Mo}^{\text{VI}}\text{–S}$  bond. The formation of the trisulphide can be represented as shown below.



In their report on the aqueous synthesis of  $\text{MoS}_3$  Wang *et al*<sup>33</sup> have shown that the  $\text{MoS}_3$  formed by the reaction of **1** with excess of dilute  $\text{H}_2\text{SO}_4$  actually contains trace amounts of  $\text{MoS}_2$  as evidenced by powder diffraction, indicating the complex nature of the acidification reaction. While the individual formation of  $[\text{Mo}_2\text{OS}_7]^{2-}$  or  $\text{MoS}_3$  can be rationalized by (2) or (3), it is still not clear as to how the initially formed Mo(V) dimer ((2)) is reoxidised to Mo(VI) in  $\text{MoS}_3$ . Further studies are essential to unravel the nature and characteristics of other transient intermediates before  $\text{MoS}_3$  is formed. The process of acidification of tetrathiomolybdate can be summarized as shown below.



As the acidification reaction did not lead to the assembling of the desired heptanuclear product but led instead to a reduced dimeric product, another method was investigated for the preparation of  $[\text{Mo}_7\text{S}_{24}]^{6-}$  complex. This method was modelled based on the synthesis of  $[\text{MoS}_4]^{2-}$  wherein the reaction of  $[\text{MoO}_4]^{2-}$  with  $\text{H}_2\text{S}$  results in the displacement of the oxo ligands by  $\text{S}^{2-}$ , leading to the formation of the corresponding tetrathio analogue. Thus the reaction of  $[\text{Mo}_7\text{O}_{24}]^{6-}$  a pre-assembled heptanuclear core was investigated by passing  $\text{H}_2\text{S}$  with a view to displacing the  $\text{O}^{2-}$  by  $\text{S}^{2-}$  leading to  $[\text{Mo}_7\text{S}_{24}]^{6-}$ . Passing of  $\text{H}_2\text{S}$  directly into an aqueous solution of ammonium heptamolybdate (pH = 5.5) resulted in the formation of a dark red reaction mixture (pH = 7.1). The reason for the increase in pH is not very clear. The optical spectrum of the reaction mixture at this stage was very characteristic of the complexes containing the dinuclear  $\{\text{Mo}_2\text{S}_4\}^{2+}$  core indicating that ligand displacement accompanied with reduction is the favoured process. The non-accessibility of any polynuclear Mo(VI)–S complexes in this reaction clearly indicates that addition of S-donor ligands on to the heptanuclear core leads to its collapse resulting in the formation of a dinuclear Mo(V) product. The addition of an organic cation like  $[(n\text{-Bu})_4\text{N}]\text{Br}$  into the reaction mixture afforded the asymmetrical oxo, sulphido Mo(V) dimer which was identified by its characteristic IR spectrum. In the absence of any added cation the reaction mixture slowly decomposed to  $\text{MoS}_3$  over several days, while acidification

at this stage resulted in the formation of black  $\text{MoS}_3$ . The formation of the dinuclear Mo(V) complex is the key factor that precludes the formation of any higher nuclearity Mo–S complexes.

### 3.4 Structural considerations

Formation of the dinuclear Mo(V) complex under the investigated reaction conditions can be explained based on the known bond distances of Mo–S complexes. Table 2 lists the reported bond lengths of some oxo and thiomolybdates. The mononuclear tetrahedral  $[\text{MoX}_4]^{2-}$  (X = O or S) complexes exhibit four terminal Mo–O or Mo–S distances at 1.795 and 2.177 Å respectively. The terminal Mo–O bond distances observed in the  $[\text{Mo}_7\text{O}_{24}]^{6-}$  complex are shorter at 1.72 Å than those observed in  $[\text{MoO}_4]^{2-}$ . Assuming that  $[\text{Mo}_7\text{S}_{24}]^{6-}$  is isomorphous with its oxo analogue, namely heptamolybdate, it is expected that the structure of the all-sulphur analogue of heptamolybdate should support a total of 32 Mo(VI)–S bonds. Of these, the twelve terminal Mo–S bond lengths should be shorter than the Mo–S distances of 2.177 Å normally observed in  $[\text{MoS}_4]^{2-}$ . Interestingly the expected shorter bond distances are observed in several Mo(V)–S complexes (table 2). For the dinuclear complexes containing the  $\{\text{Mo}_2\text{S}_4\}^{2+}$  core only the terminal Mo(V)–S lengths are shown and these distances range from 2.092 to 2.129 Å. It is pertinent to note that these distances do not vary much even when the other ligands around Mo are changed. The observation of shorter Mo–S bonds in the dinuclear Mo(V) complexes is indicative of the fact that a closer approach of S to Mo results in electron transfer and consequently reduction of Mo(VI) to Mo(V). This feature is not surprising because electron transfer across the Mo–S bond is a well known phenomenon<sup>41–43</sup> and indeed the formation of several Mo–S compounds, especially the dinuclear complexes like  $[\text{Mo}_2\text{S}_3\text{O}(\text{S}_2)_2]^{2-}$ ,  $[\text{Mo}_2\text{S}_4(\text{S}_2)_2]^{2-}$ ,  $[\text{Mo}_2\text{S}_2\text{O}_2(\text{S}_2)_2]^{2-}$ , has been explained based on such electron transfer.<sup>39,41,42</sup> While the formation of the  $[\text{Mo}_2\text{OS}_7]^{2-}$  complex can be rationalized in terms of the shorter Mo–S bond distances, the same argument can also be extended to explain the non-accessibility of  $[\text{Mo}_7\text{S}_{24}]^{6-}$ . The structural requirements of  $[\text{Mo}_7\text{S}_{24}]^{6-}$  demands twelve Mo–S bonds at shorter distances than in  $[\text{MoS}_4]^{2-}$ , which cannot be met, as the closer approach of S to Mo leads to electron transfer resulting in the collapse of the heptanuclear Mo(VI) structure. This argument gains

**Table 2.** Selected bond distances  $d$ , number of Mo–S (term) of distances  $n$ , of a few oxo and thiomolybdates<sup>a</sup>.

Complex	Bond	$d$ (in Å)	$n$	Ref.
[MoO <sub>4</sub> ] <sup>2-</sup>	Mo(VI)–O (term)	1.795	4	56
[Mo <sub>7</sub> O <sub>24</sub> ] <sup>6-</sup>	Mo(VI)–O (term)	1.72	12	17
	Mo(VI)–O (br)	1.93	14	
	Mo(VI)–O (br)	2.27	6	
	Mo(VI)–S (term)	2.177	4	57
[MoS <sub>4</sub> ] <sup>2-</sup>	Mo(VI)–S (term)	–	12	–
[Mo <sub>7</sub> S <sub>24</sub> ] <sup>6-</sup>	Mo(VI)–S (br)	–	14	
	Mo(VI)–S (br)	–	6	
	Mo(V)–S (term)	2.118	2	41
[Mo <sub>2</sub> S <sub>4</sub> (S <sub>2</sub> ) <sub>2</sub> ] <sup>2-</sup>	Mo(V)–S (term)	2.11	1	39
[Mo <sub>2</sub> S <sub>3</sub> O(S <sub>2</sub> ) <sub>2</sub> ] <sup>2-</sup>	Mo(V)–S (term)	2.110	2	58
[Mo <sub>2</sub> S <sub>4</sub> (S <sub>2</sub> )(S <sub>4</sub> )] <sup>2-</sup>	Mo(V)–S (term)	2.118	2	59
[Mo <sub>2</sub> S <sub>4</sub> (S <sub>4</sub> )(S <sub>4</sub> )] <sup>2-</sup>	Mo(V)–S (term)	2.100	2	60
[Mo <sub>2</sub> S <sub>4</sub> (edt) <sub>2</sub> ] <sup>2-</sup>	Mo(V)–S (term)	2.129	2	60
[Mo <sub>2</sub> S <sub>4</sub> (edt) <sub>2</sub> ] <sup>2-</sup> #	Mo(V)–S (term)	2.092	2	61
[Mo <sub>2</sub> S <sub>4</sub> (Et-dtc) <sub>2</sub> ]	Mo(V)–S (term)	2.100	2	62
[Mo <sub>2</sub> S <sub>4</sub> (CS <sub>4</sub> ) <sub>2</sub> ] <sup>2-</sup>	Mo(V)–S (term)	2.108	2	62
[Mo <sub>2</sub> S <sub>4</sub> (CS <sub>3</sub> ) <sub>2</sub> ] <sup>2-</sup>	Mo(V)–S (term)			

<sup>a</sup>Abbreviations: term = terminal; br = bridging; {Mo<sub>2</sub>S<sub>4</sub>} = [(S)Mo(*m*-S)<sub>2</sub>Mo(S)]<sup>2+</sup>; edt = ethanedithiolate; #anti isomer; Et-dtc = N,N'-diethyldithiocarbamate

credence based on the results of the direct reaction of H<sub>2</sub>S with [Mo<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> (vide supra). To the best of my knowledge there is no report of a Mo(VI)–S terminal bond in any complex at around 2.11 Å. In contrast, the closer approach of the oxide ligands in [Mo<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> does not induce electron transfer across the Mo–O bond and consequently this complex is stable and can be isolated. It is well known that the hard O<sup>2-</sup> ligand can stabilize (coexist with) higher oxidation states of metal. Thus the structural aspects of Mo–S complexes indicate that the all-sulphur analogue of heptamolybdate with several Mo–S(term) bonds at shorter distances than in [MoS<sub>4</sub>]<sup>2-</sup> is not stable and is prone to internal redox reactions. In the absence of theoretical evidence to further support this fact, it will be premature to label the [Mo<sub>7</sub>S<sub>24</sub>]<sup>6-</sup> complex as a non-existent complex. However, based on the present results it can be stated that this complex cannot exist in an alkaline medium and also cannot be isolated from an aqueous acidic medium.

#### 4. Conclusions

Dianionic [MoX<sub>4</sub>]<sup>2-</sup> (X = O or S) complexes exist as the monomeric tetrahedral species in aqueous alkaline solutions. Reaction of an ammoniacal molyb-

date solution with H<sub>2</sub>S results in the formation of (NH<sub>4</sub>)<sub>2</sub>[MoS<sub>4</sub>] **1**. Passing H<sub>2</sub>S gas for extended periods does not result in the formation of any polynuclear Mo–S complex other than [MoS<sub>4</sub>]<sup>2-</sup>. All attempts to prepare **2** by acidification (with excess acid) of (NH<sub>4</sub>)<sub>2</sub>[MoS<sub>4</sub>] **1** results in the formation of the insoluble MoS<sub>3</sub>. The first product of acidification of [MoS<sub>4</sub>]<sup>2-</sup> is the dinuclear complex [Mo<sub>2</sub>OS<sub>7</sub>]<sup>2-</sup>. The same complex can also be prepared by directly passing H<sub>2</sub>S into an aqueous ammonium heptamolybdate solution (pH = 5.5) indicating the difference in the nature of the Mo–S product formed, depending upon the medium pH. Formation of the reduced dinuclear Mo(V) complex instead of the all-sulphur analogue of heptamolybdate is explained based on bond distances or closer approach of S to Mo. Formation of the dinuclear Mo(V) complex precludes the formation of any higher nuclearity Mo–S complexes in aqueous solution. The all-sulphur analogue of heptamolybdate **2** cannot exist in an alkaline medium and also cannot be isolated from an aqueous acidic medium.

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