

# Reversible Hydration Characteristics of Group VI Tetrathiomallates Derived from Tris(2-aminoethyl)amine

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## Abstract

The complexes (trenH<sub>2</sub>)[MoS<sub>4</sub>]·H<sub>2</sub>O **1** and (trenH<sub>2</sub>)[WS<sub>4</sub>]·H<sub>2</sub>O **2** (tren = tris(2-aminoethylamine)) were synthesized by the base promoted cation exchange method. Both complexes can be dehydrated to the corresponding anhydrous compounds (trenH<sub>2</sub>)[MS<sub>4</sub>] (M = Mo **3**; W **4**) and the anhydrous complexes can be rehydrated. This reversible hydration behaviour has been investigated by isothermal weight loss studies, IR spectroscopy, TG-DTA studies and X-ray measurements. On heating, complexes **1** and **2** emit crystal water forming the corresponding anhydrous complexes **3** and **4**. Equilibration of the anhydrous complexes over aqueous ammonia, results in the formation of the monohydrates **1** and **2**. The complexes **3** and **4** are isostructural as evidenced from the IR and X-ray studies. At elevated temperatures, all the tetrathiomallates decompose to yield carbon contaminated amorphous metal disulfides.

## Introduction

It is well documented that the tetrahedral [MS<sub>4</sub>]<sup>2-</sup> unit is an important building block that can be used to generate several Mo/W-S complexes [1]. The use of (NH<sub>4</sub>)<sub>2</sub>[MS<sub>4</sub>] (M = Mo, W) as precursors for the soft synthesis of WS<sub>2</sub> nanotubes is responsible for the recent interest in the chemistry of tetrathiomallates [2]. As part of an overall programme aimed at the synthesis of novel metal-sulfide materials we are investigating the synthesis and structural characterization of organic ammonium tetrathiotungstates and the corresponding tetrathiomolybdates and have structurally characterized several new complexes [3-7]. The compounds derived from the tetraamine tris(2-aminoethylamine) tren are the first examples of structurally characterized hydrated tetrathiomallates recently reported by us [5] and undergo the interesting phenomenon of reversible hydration as evidenced by the present investigations. The results of these studies are described in this paper.

## Experimental

All chemicals were used in this work as obtained from commercial sources. The details of the instrumentation used in this investigation were the same as described in our earlier reports [4,5].

### Preparation of complexes 1-4

The complexes **1** and **2** were synthesized in good yields by reacting an aqueous solution of  $(\text{NH}_4)_2[\text{MS}_4]$  ( $\text{M} = \text{Mo}, \text{W}$ ) with the organic tetraamine tris(2-aminoethyl)amine (tren) as reported earlier [5]. Powdered samples of  $(\text{trenH}_2)[\text{MoS}_4] \cdot \text{H}_2\text{O}$  **1** (400 mg) or  $(\text{trenH}_2)[\text{WS}_4] \cdot \text{H}_2\text{O}$  **2** (300 mg) were heated separately in an electric furnace at  $130^\circ\text{C}$  and  $140^\circ\text{C}$  respectively. This resulted in the formation of the anhydrous  $(\text{trenH}_2)[\text{MoS}_4]$  **3** (381.5 mg) and  $(\text{trenH}_2)[\text{WS}_4]$  **4** (288.8 mg). The complexes **3** and **4** were equilibrated over aqueous ammonia in a desiccator for about 2 h to obtain the original monohydrates **1** and **2** respectively as described in equation 1. All the complexes **1-4** are freely soluble in aqueous ammonia, DMSO, DMF etc.



### Results and Discussion

All the four complexes **1-4** were characterized by analysis, IR, TG-DTA, and X-ray powder diffraction measurements. The IR spectra (Fig 1 & 2) of all the complexes exhibit several intense peaks in the mid IR region, which can be attributed to the tren moiety. The intense signals in the region  $450\text{-}500\text{ cm}^{-1}$  are characteristic of the vibrations arising from the  $\text{MS}_4$  tetrahedron. The broad signals at  $3462\text{ cm}^{-1}$  in **1** and  $3471\text{ cm}^{-1}$  in **2** can be assigned to the O-H vibrations of the crystal water. On heating, complex **1** emits crystal water at about  $130^\circ\text{C}$  while **2** loses water at  $140^\circ\text{C}$  forming anhydrous  $(\text{trenH}_2)[\text{MoS}_4]$  **3** and  $(\text{trenH}_2)[\text{WS}_4]$  **4** respectively. The mass losses of 4.62 % in **1** and 3.73 % in **2** at these temperatures are in good agreement with the expected values for the loss of one mole of water. A strong endothermic peak at  $113^\circ\text{C}$  in **1** and at  $103^\circ\text{C}$  in **2** is observed for the elimination of water forming the anhydrous complexes **3** and **4**. The TG-DTA traces of anhydrous **3** and **4** are depicted in Fig 3 & 4. On heating, complex **3** starts decomposing accompanied by endothermic events at  $154$  and  $198^\circ\text{C}$ . These temperatures are in well accordance for the decomposition organic amine with endothermic peaks at  $162$  and  $203^\circ\text{C}$  in **1**. Complex **4** behaves similarly. On heating from room temperature, TG curves of **3** and **4** are parallel to the horizontal axis till at around  $140^\circ\text{C}$  indicating no mass loss in this range. No endothermic peaks like in **1** and **2** for elimination of water were observed in the DTA curves of **3** and **4**. The IR spectra of **3** and **4** are nearly identical to those of **1** and **2** except in the region  $3500\text{-}3000\text{ cm}^{-1}$ . (Fig 1 & 2). The broad bands due to water in **1** and **2** are not observed in **3** and **4** indicating the complete removal of crystal water at these

temperatures. The X-ray powder pattern of **3** and **4** are quite different from those of **1** and **2** suggesting the formation altogether different phases. The calcined samples of **1** or **2** can be rehydrated, as evidenced by the IR, and X-ray powder pattern. Both **3** and **4** when equilibrated over water-ammonia atmosphere reabsorb the emitted water to form the original phases. Equilibration over only water takes considerably long time for the rehydration and the use of ammonia hastens the rehydration in view of the enhanced solubility in ammonia. The IR spectra of the rehydrated samples are identical to that of **1** and **2** showing the reappearance of -OH bands due to absorbed water. This phenomenon of reversible hydration leading to original phases can also be evidenced from the X-ray powder patterns displayed in Fig 5 & 6. Heating of **1-4** at around 600 °C results in the formation of carbon contaminated molybdenum and tungsten sulfides.

### **Conclusions:**

The thermal and spectroscopic characterization of organic tetrathiomallates derived from tren are reported. The hydrated tren salts of the group VI tetrathiomallates can be dehydrated and the anhydrous compound rehydrated on exposure to aqueous ammonia.

### **Acknowledgements**

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### **References**

1. A. Müller, E. Diemann, R. Jostes and H. Bögge, *Angew. Chem. Int. Ed. Engl.* 20 (1981) 934; T. Shibahara, *Coord. Chem. Rev.* 123 (1993) 73.
2. M. Nath, A. Govindaraj and C. N. R. Rao, *Adv. Mater.* 13 (2001) 283; J. Chen, S. L. Li, F. Gao and Z. L. Tao, *Chem. Mater.* 15 (2003) 1012.
3. B. R. Srinivasan, S. N. Dhuri, C. Näther and W. Bensch, *Monats. Chem.*, (2005) (in press).
4. B. R. Srinivasan, S. N. Dhuri, C. Näther and W. Bensch, *Inorg. Chim Acta.* 358 (2005) 279.
5. B. R. Srinivasan, S. N. Dhuri, M. Poisot, C. Näther and W. Bensch, *Z. Anorg. Allg. Chem.* 631 (2005) 1087; *Z. Naturforsch.* 59b (2004) 1083.
6. B. R. Srinivasan, S. N. Dhuri, C. Näther and W. Bensch, *Acta Cryst.* C59 (2003) m124; *Acta Cryst.* E59 (2003) m681; *Acta Cryst.* E58 (2002) m622.
7. B. R. Srinivasan, B. K. Vernekar and K. Nagarajan, *Indian J. Chem.* 40A (2001) 563.

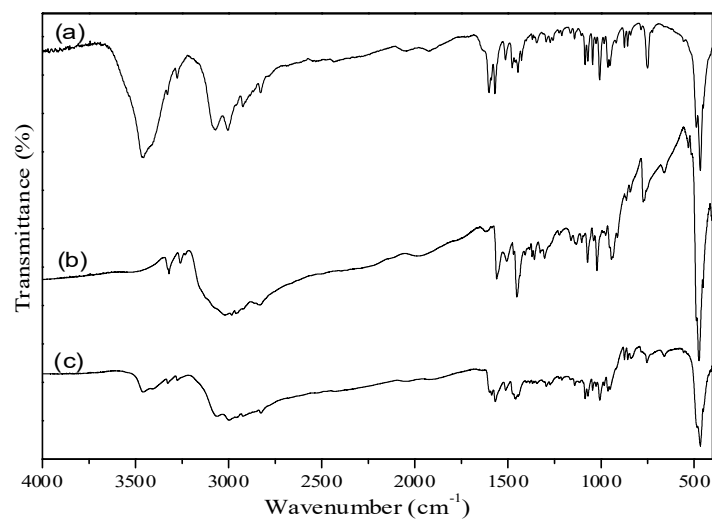


Fig. 1 IR spectra of (a)  $(\text{trenH}_2)[\text{MoS}_4] \cdot \text{H}_2\text{O}$  **1** (b) anhydrous  $(\text{trenH}_2)[\text{MoS}_4]$  **3** (c) rehydrated  $(\text{trenH}_2)[\text{MoS}_4] \cdot \text{H}_2\text{O}$

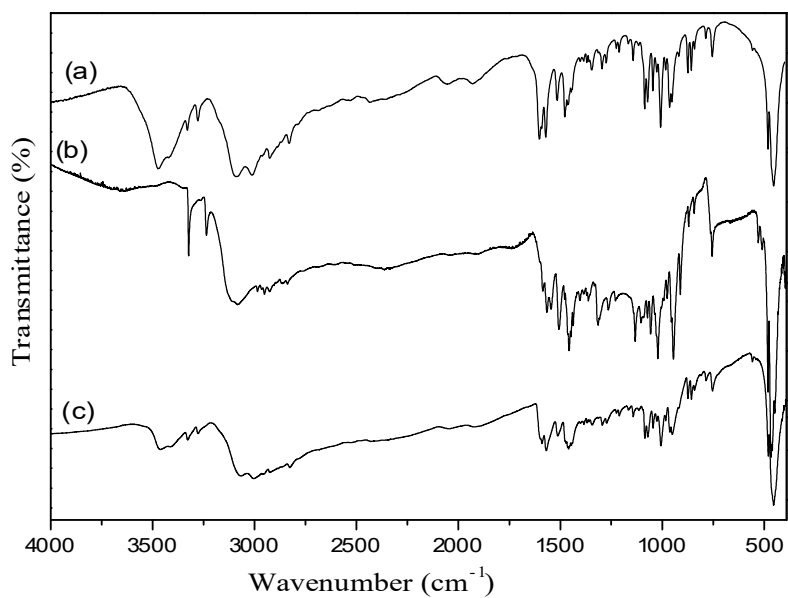


Fig 2. IR spectra of (a)  $(\text{trenH}_2)[\text{WS}_4] \cdot \text{H}_2\text{O}$  **2** (b) anhydrous  $(\text{trenH}_2)[\text{WS}_4]$  **4** (c) rehydrated  $(\text{trenH}_2)[\text{WS}_4] \cdot \text{H}_2\text{O}$

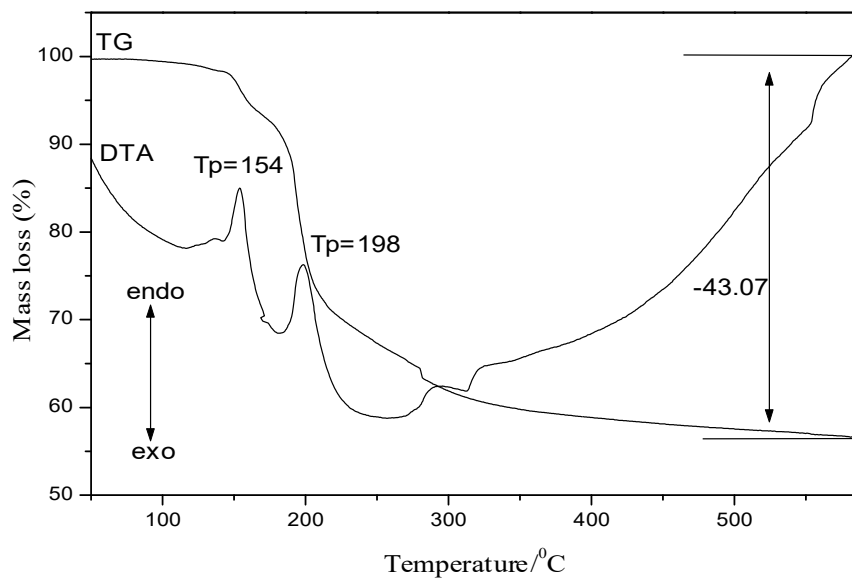


Fig 3. TG-DTA trace for  $(\text{trenH}_2)[\text{MoS}_4]$  **3** (heating rate 4 K/min; Ar atmosphere,  $T_p$  = peak temperature in  $^\circ\text{C}$ )

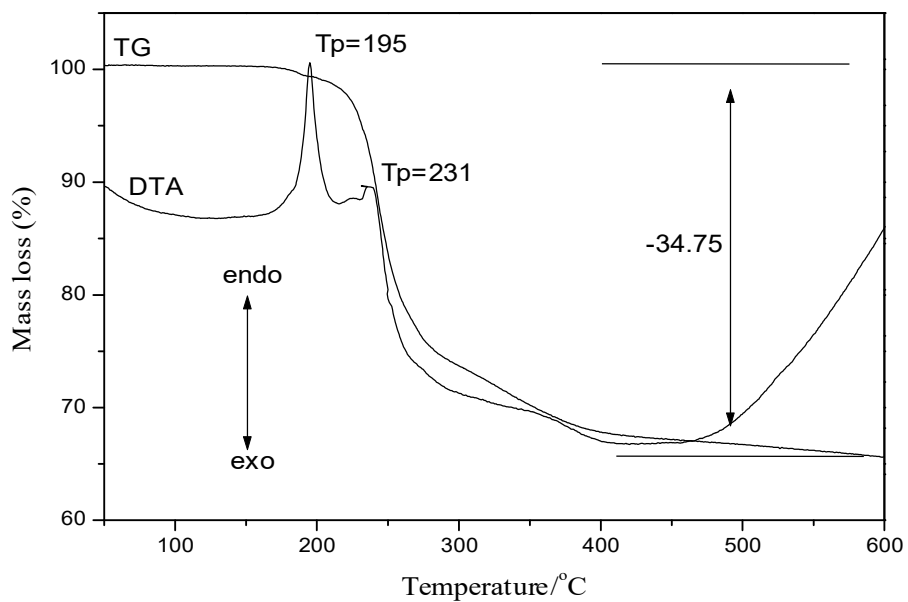


Fig 4. TG-DTA curves for anhydrous  $(\text{trenH}_2)[\text{WS}_4]$  **4** (heating rate 4 K/min; Ar atmosphere;  $T_p$  = peak temperatures in  $^\circ\text{C}$ ).

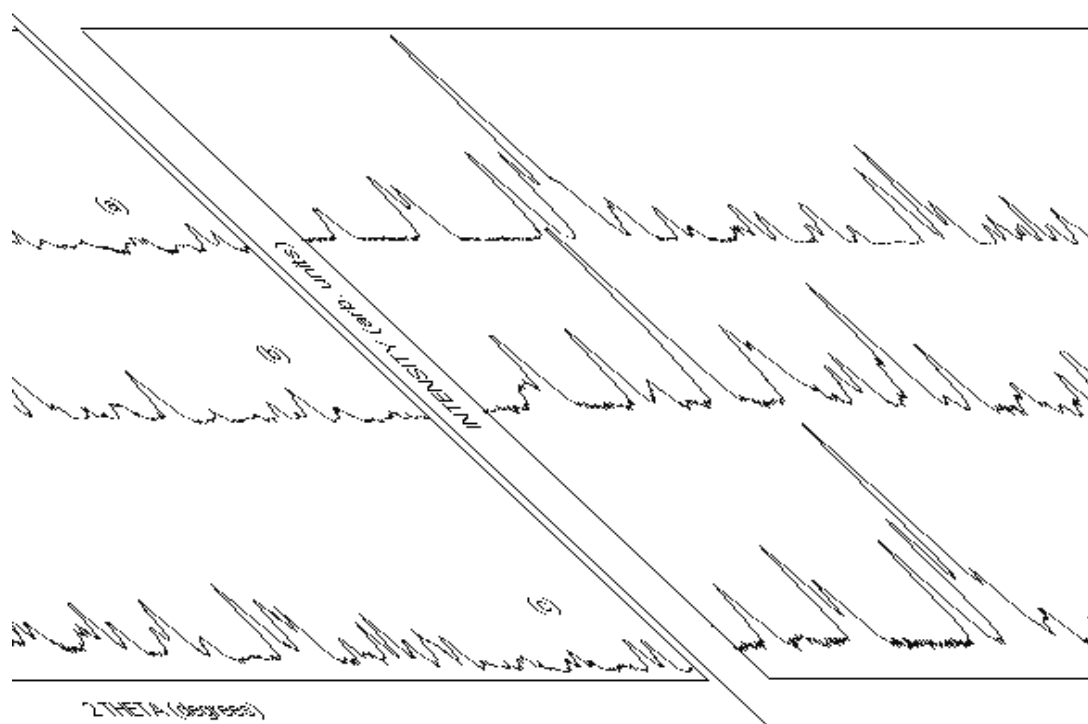


Fig 5. X-ray powder pattern of (a) pristine  $(\text{trenH}_2)[\text{MoS}_4]\cdot\text{H}_2\text{O}$  **1** (b) anhydrous  $(\text{trenH}_2)[\text{MoS}_4]$  **3** (c) rehydrated  $(\text{trenH}_2)[\text{MoS}_4]\cdot\text{H}_2\text{O}$

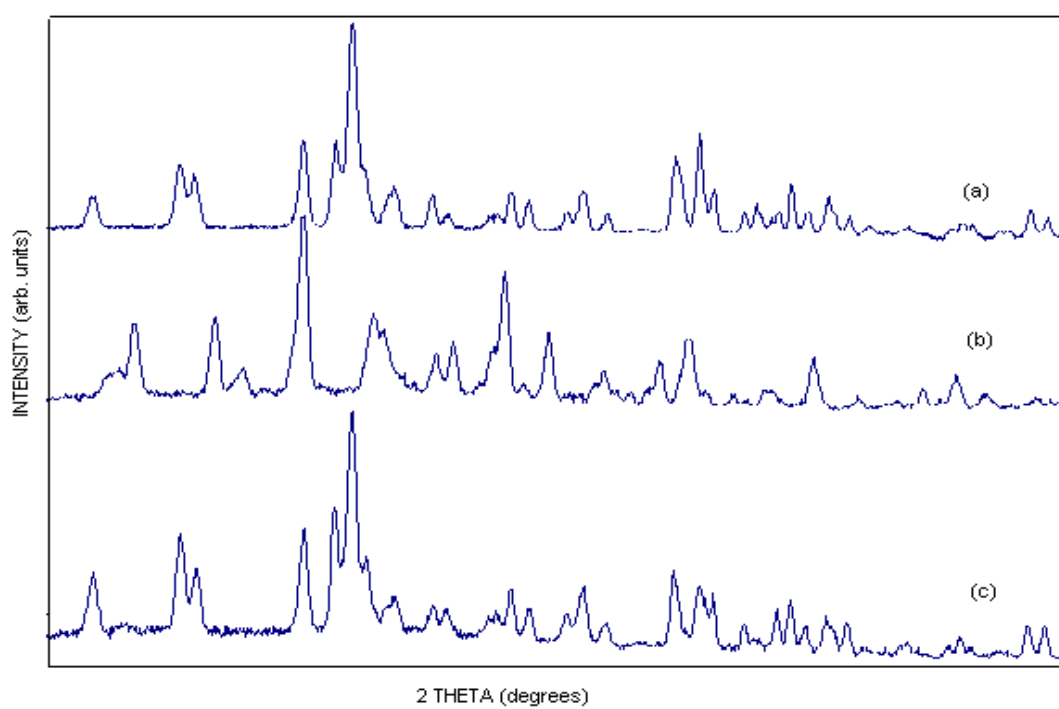


Fig 6. X-ray powder pattern of (a) pristine  $(\text{trenH}_2)[\text{WS}_4]\cdot\text{H}_2\text{O}$  **2** (b) anhydrous  $(\text{trenH}_2)[\text{WS}_4]$  **4** (c) rehydrated  $(\text{trenH}_2)[\text{WS}_4]\cdot\text{H}_2\text{O}$