CHAPTER 2
EXPERIMENTAL DETAILS

2.1 General considerations

Materials and methods

All reactions were carried out using double distilled water as a solvent, unless specified otherwise. All the chemicals such as organic amines, organic solvents and mineral acids were used as obtained from commercial sources. The compounds such as (NH₄)₂[MoS₄] [16], (NH₄)₂[WS₄] [16], [Ni(en)₃]Cl₂·2H₂O [157] were prepared by literature methods. Hydrogen sulfide gas was generated by adding dilute hydrochloric acid to ferrous sulfide sticks (CAUTION: H₂S gas, organic amines and mineral acids used in this work have been handled with the appropriate precautions). The pH of the solutions were determined using short-range pH paper as well as electronic pH meter (Model PHAN, Lab India). The mid-IR spectra of the samples were recorded on a IR Prestige-21 Fourier transform (SHIMADZU) (4000-250 cm⁻¹) infrared (IR) spectrometers at Department of Chemistry, Goa University and ATI Mattson Genesis (range 450-3000 cm⁻¹) (resolution 1 cm⁻¹) IR spectrometer at the Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel. The mid-IR spectra of the compounds were recorded in a KBr matrix, while far-IR spectra (range 80 to 500 cm⁻¹) were measured on a Bruker IFS 66 infrared spectrometer in pressed polyethylene discs. Raman spectra were measured in the region 100-3500 cm⁻¹ on a Bruker FRA106 FT Raman spectrometer. UV-Visible (electronic) spectra of sulfidometalates in dilute ammonia and chromates in water were recorded using matched quartz cuvettes on a Varian Cary 5 UV-VIS-NIR equipment and Shimadzu UV-1601 instrument. The C, H, N and S analyses were performed on a HEKA Tech Euro EA elemental analyzer. Thermal decomposition studies were performed in an electric furnace (Newtronic) fitted with a temperature controller in silica crucibles. TG-DTA measurements were performed simultaneously using the STA-409CD device (Netzsch). The thermal investigations were performed in Al₂O₃ crucibles using a heating rate of 4 °K/min and purged in a N₂ and Ar stream of 75 ml/min. EDX analysis was performed with a Philips ESEM XL 30 scanning electron microscope equipped with an EDAX analyzer. X-ray powder patterns were recorded in
transmission geometry using a STOE STADI P diffractometer (CuK$_\alpha$ = 1.54056 Å) at Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Germany.

2.2 Synthetic Procedures for sulfidometalates

2.2.1 Preparation of (NH$_4$)$_2$[MS$_4$] (M = Mo, W)

a. Synthesis of (NH$_4$)$_2$[MoS$_4$] [16]

Ammonium heptamolybdate (3 g) was dissolved in water (5 ml) and ammonia (25 ml) mixture to obtain a clear solution (pH=12.1). A rapid stream of H$_2$S gas was passed into this solution for ~30 min and the temperature was maintained at 60 °C. The H$_2$S gas flow was stopped as the crystal started to appear and the reaction mixture was left undisturbed to attain room temperature. The mixture was then cooled in an ice bath for ~1 h. The crystals obtained were isolated by filtration and washed well with isopropyl alcohol (25 ml) followed by diethyl ether (25 ml). The compound was stored in a vacuum dessicator. Yield (4.3 g). Anal. Found (calc.) for N$_2$H$_8$MoS$_4$: (NH$_4$) 13.85 (13.87), Mo 36.70 (36.85), S 49.11 (49.28), MoS$_4$ 85.85 (86.23).

b. Synthesis of (NH$_4$)$_2$[WS$_4$] [16]

A white slurry of tungstic acid H$_2$[WO$_4$] (10 g) with water (20 ml) and ammonia (50 ml) was made and into this solution a continuous and rapid stream of H$_2$S gas was passed for about 8 h and the temperature was maintained at 60 °C. After 8 h, the mixture was filtered, and left undisturbed in a refrigerator to obtain yellow blocks of (NH$_4$)$_2$[WS$_4$]. The compound was isolated by filtration, washed well with isopropyl alcohol (30 ml) followed by diethyl ether (25 ml) and dried under vacuum. Yield (6 g). Anal. Found (calc.) for N$_2$H$_8$WS$_4$: WS$_4$ 88.99 (89.65) %.

2.2.2 Preparation of (CH$_3$NH$_3$)$_2$[MoS$_4$] 1 and (CH$_3$NH$_3$)$_2$[WS$_4$] 2

Molybdic acid (3 g) was dissolved in a mixture of 40% methyl amine (10 ml) and distilled water (5 ml). A rapid stream of H$_2$S gas was bubbled into this for 30 min at 60 °C, resulting in the formation of a red solid. The reaction mixture was cooled to room temperature and the red solid filtered off. The filtrate was left aside at room temperature for 2 d, resulting in the formation of crystalline blocks of the title compound used for the structure determination. The crystals were isolated by
filtration, washed with isopropyl alcohol (20 ml) followed by diethyl ether (20 ml), and dried under vacuum. Yield (2.9 g). Anal. Found (calc.) for \( \text{I} \) (\( \text{C}_2\text{H}_12\text{N}_2\text{MoS}_4 \)): C 8.30 (8.33), H 4.22 (4.20), N 9.80 (9.72), S 44.38 (44.48), MoS\(_4\) 77.33 (77.75) %.

**Compound 2**

\( (\text{NH}_4)_2[\text{WS}_4] \) (1 g) was dissolved in water (2 ml) and 40% methyl amine (5 ml) and kept for crystallization. After a week yellow crystal were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (20 ml) followed by diethyl ether (20 ml), and dried under vacuum. Yield (1.1 g). Anal. Found (calc.) for \( \text{II} \) (\( \text{C}_2\text{H}_12\text{N}_2\text{WS}_4 \)): C 6.41 (6.38), H 3.20 (3.22), N 7.42 (7.45), S 34.00 (34.09), WS\(_4\) 82.28 (82.95) %.

Both \( \text{I} \) and \( \text{II} \) are fairly stable in air, soluble in water, freely soluble in ammonia, DMSO, DMF and insoluble in CH\(_3\)CN, CH\(_2\)Cl\(_2\), toluene, alcohol etc.

### 2.2.3 Preparation of \( (\text{C}_2\text{H}_5\text{NH}_3)_2[\text{MoS}_4] \) \( \text{III} \) and \( (\text{C}_2\text{H}_5\text{NH}_3)_2[\text{WS}_4] \) \( \text{IV} \)

Molybdic acid (1.6 g) was dissolved in a mixture of 70% ethyl amine (6 ml) and distilled water (15 ml). A rapid stream of H\(_2\)S gas was bubbled into this for 30 min at 60 °C, resulting in the formation of a red solid. The reaction mixture was cooled to room temperature and the red solid filtered off. The filtrate was left aside at room temperature for 2 d, resulting in the formation of crystalline blocks. The crystals were isolated by filtration, washed with isopropyl alcohol (20 ml) followed by diethyl ether (20 ml), and dried under vacuum. Yield (1.7 g). Anal. Found (calc.) for \( \text{III} \) (\( \text{C}_4\text{H}_16\text{N}_2\text{MoS}_4 \)): C 15.00 (15.18), H 5.10 (5.11), N 8.68 (8.85), S 40.52 (40.54), MoS\(_4\) 70.30 (70.86) %.

**Compound 4**

\( (\text{NH}_4)_2[\text{WS}_4] \) (1 g) was dissolved in water (2 ml) and 70% ethyl amine (3.5 ml) and kept for crystallization. After few days yellow crystal were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (20 ml) followed by diethyl ether (20 ml), and dried under vacuum. Yield (1.2 g). Anal. Found (calc.) for \( \text{IV} \) (\( \text{C}_4\text{H}_16\text{N}_2\text{WS}_4 \)): C 11.81 (11.88), H 4.02 (4.00), N 6.92 (6.93), S 31.80 (31.72), WS\(_4\) 77.01 (77.19) %.

Both \( \text{III} \) and \( \text{IV} \) are fairly stable in air, soluble in water and freely soluble in ammonia, DMSO, DMF and insoluble in CH\(_3\)CN, CH\(_2\)Cl\(_2\), toluene, alcohol etc.
2.2.4 Preparation of (n-C₃H₇NH₃)₂[MoS₄] 5 and (n-C₃H₇NH₃)₂[WS₄] 6

Molybdic acid (2 g) was dissolved in a mixture of n-propylamine (4 ml) and distilled water (15 ml). A rapid stream of H₂S gas was bubbled into this for 30 min at 60 °C, resulting in the formation of a red solid. The reaction mixture was cooled to room temperature and the red solid filtered off. The filtrate was left aside at room temperature for 2 d, resulting in the formation of crystalline blocks of the title compound used for the structure determination. The crystals were isolated by filtration, washed with isopropyl alcohol (20 ml) followed by diethyl ether (20 ml), and dried under vacuum. Yield (2.8 g). Anal. Found (calc.) for 5 (C₆H₂₀N₂MoS₄): C 20.63 (20.92), H 5.83 (5.86), N 8.17 (8.13), S 37.02 (37.24), MoS₄ 65.21 (65.09) %.

Compound 6

(NH₄)₂[WS₄] (348 mg) was dissolved in water (15 ml) and into this added 7 drops of n-propylamine. After a week, yellow crystals were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (10 ml) followed by diethyl ether (10 ml), and dried under vacuum. Yield (0.17 g). Anal. Found (calc.) for 6 (C₆H₂₀N₂WS₄): C 16.85 (16.66), H 4.63 (4.67), N 6.71 (6.48), S 29.31 (29.67), WS₄ 72.08 (72.19) %.

Both 5 and 6 are stable in air, soluble in water, freely soluble in ammonia, DMSO, DMF and insoluble in CH₃CN, CH₂Cl₂, toluene, alcohol etc. The crystals obtained by this method were suitable for X-ray studies.

2.2.5 Preparation of (n-C₄H₉NH₃)₂[MoS₄] 7 and (n-C₄H₉NH₃)₂[WS₄] 8

Molybdic acid (2 g) was dissolved in a mixture of n-butyramine (6 ml) and distilled water (5 ml). A rapid stream of H₂S gas was bubbled into this for 30 min at 60 °C, resulting in the formation of a red solid. The reaction mixture was cooled to room temperature and the red solid filtered off. The filtrate was left aside at room temperature for 2 d, resulting in the formation of crystalline blocks. The crystals were isolated by filtration, washed with isopropyl alcohol (20 ml) followed by diethyl ether (20 ml), and dried under vacuum. Yield (3.65 g). Anal. Found (calc.) for 7 C₈H₁₈N₂MoS₄: C 25.08 (25.79), H 6.45 (6.51), N 7.49 (7.52), S 34.23 (34.43), MoS₄ 60.49 (60.18) %.
Compound 8

(NH₄)₂[WS₄] (348mg) was dissolved in water (15 ml) and into this added 0.4ml of n-butylamine. After a week, yellow crystals were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (10 ml) followed by diethyl ether (10 ml), and dried under vacuum. Yield (0.22 g). Anal. Found (calc.) for 8 C₈H₂₄N₂WS₄: C 20.78 (20.87), H 5.30 (5.26), N 6.12 (6.09), S 27.82 (27.86), WS₄ 67.88 (67.79) %.

Both 7 and 8 are stable in air, soluble in water, freely soluble in ammonia, DMSO, DMF and insoluble in CH₃CN, CH₂Cl₂, toluene, alcohol etc.

2.2.6 Preparation of (t-C₄H₉NH₃)₂[MoS₄] 9 and (t-C₄H₉NH₃)₂[WS₄] 10

Molybdic acid (2 g) was dissolved in a mixture of t-butylamine (6 ml) and distilled water (15 ml). A rapid stream of H₂S gas was bubbled into this for 30 min at 60 °C, resulting in the formation of a red solid. The reaction mixture was cooled to room temperature and the red solid filtered off. The filtrate was left aside at room temperature for 2 d, resulting in the formation of crystalline blocks. The crystals were isolated by filtration, washed with isopropyl alcohol (20 ml) followed by diethyl ether (20 ml), and dried under vacuum. Yield (3.05 g). Anal. Found (calc.) for 9 C₈H₂₄N₂MoS₄: C 25.57 (25.79), H 6.35 (6.51), N 7.36 (7.52), S 34.40 (34.43), MoS₄ 60.38 (60.18) %.

Compound 10

(NH₄)₂[WS₄] (348mg) was dissolved in water (15 ml) and into this added 0.4ml of t-butylamine. After a week, yellow crystals were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (10 ml) followed by diethyl ether (10 ml), and dried under vacuum. Yield (0.21 g). Anal. Found (calc.) for 10 C₈H₂₄N₂WS₄: C 20.80 (20.87), H 5.24 (5.26), N 6.01 (6.09), S 27.80 (27.86), WS₄ 67.96 (67.79) %.

Both 9 and 10 are stable in air, slightly soluble in water, freely soluble in ammonia, DMSO, DMF and insoluble in CH₃CN, CH₂Cl₂, toluene, alcohol etc. The
crystals obtained by this method were suitable for single crystal structure determination.

2.2.7 Preparation of (iso-C\textsubscript{3}H\textsubscript{7}NH\textsubscript{3})\textsubscript{2}[MoS\textsubscript{4}] 11 and (trans-cyclohexane-1,4-diammonium)[WS\textsubscript{4}] 12

Molybdic acid (3 g) was dissolved in a mixture of iso-propylamine (10 ml) and distilled water (30 ml). A rapid stream of H\textsubscript{2}S gas was bubbled into this for 30 min at 60 °C, resulting in the formation of a red solid. The reaction mixture was cooled to room temperature and the red solid filtered off. The filtrate was left aside at room temperature for 2 d, resulting in the formation of crystalline blocks. The crystals were isolated by filtration, washed with isopropyl alcohol (20 ml) followed by diethyl ether (20 ml), and dried under vacuum. Yield (3.2 g). Anal. Found (calc.) for 11 (C\textsubscript{6}H\textsubscript{20}N\textsubscript{2}MoS\textsubscript{4}): C 20.75 (20.92), H 5.80 (5.86), N 8.04 (8.13), S 37.22 (37.24), MoS\textsubscript{4} 65.03 (65.09) %. The crystals obtained in this method were used for X-ray analysis.

Compound 12

(NH\textsubscript{4})\textsubscript{2}[WS\textsubscript{4}] (348mg) was dissolved in water (15 ml) and into this added aqueous solution of trans-cyclohexane-1,4-diamine (114mg was added in 2ml water). After a week, yellow crystals were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (10 ml) followed by diethyl ether (10 ml), and dried under vacuum. Yield (0.3 g). Anal. Found (calc.) for 12 C\textsubscript{6}H\textsubscript{16}N\textsubscript{2}WS\textsubscript{4}: C 16.79 (16.82), H 5.21 (5.26), N 6.06 (6.09), S 27.79 (27.86), WS\textsubscript{4} 73.03 (72.87) %.

2.2.8 Preparation of [PhCH\textsubscript{2}NH\textsubscript{3}]\textsubscript{2}[MoS\textsubscript{4}] 13 and [PhCH\textsubscript{2}NH\textsubscript{3}]\textsubscript{2}[WS\textsubscript{4}] 14,

(NH\textsubscript{4})\textsubscript{2}[MoS\textsubscript{4}] (529 mg) was dissolved in water (25 ml) containing few drops of ammonia, filtered and to the red coloured solution, benzylamine (1 ml dissolved in 5ml water) was added. This resulted in the immediate separation of compound 13 (260 mg). The polycrystalline material was filtered, washed with 2-propanol (15 ml) and diethyl ether (15 ml). The filtrate was left aside for crystallization. After a week, needle shaped crystals of compound 13 (170 mg) suitable for structure determination were obtained. The crystals were filtered off and washed with 2-propanol and diethyl ether. Anal. Found (calc.) for 13 C\textsubscript{14}H\textsubscript{16}N\textsubscript{2}MoS\textsubscript{4}: C 38.62 (38.16), H 4.60 (4.58), N 7.32 (6.36), S 29.99 (29.12)%

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Compound 14 was prepared using similar synthetic procedure. Here instead of (NH₄)₂[MoS₄], (NH₄)₂[WS₄] (348 mg, dissolved in 10 ml of water) was treated with benzylamine (0.5 ml dissolved in 5 mL water). Yield (250 mg). Anal. Found (calc.) for 14 C₁₄H₁₆N₂WS₄: C 32.12 (31.82), H 3.80 (3.82), N 6.09 (5.30), S 24.52 (24.27) %.

2.2.9 Preparation of R-[PhCH(CH₃)NH₃]₂[MoS₄] 15, R-[PhCH(CH₃)NH₃]₂[WS₄] 16, S-[PhCH(CH₃)NH₃]₂[MoS₄], 17 S-[PhCH(CH₃)NH₃]₂[WS₄] 18

(NH₄)₂[MoS₄] (260 mg) was dissolved in water (12 ml) containing few drops of ammonia, filtered and to the red coloured solution, (R)(+)-α-methylbenzylamine (0.4 ml) was added. This resulted in the immediate separation of compound 13 (190 mg). The polycrystalline material was filtered, washed with 2-propanol (15 ml) and diethyl ether (15 ml). The filtrate was left aside for crystallization. After a week, needle shaped crystals of compound 15 (110 mg) suitable for structure determination were obtained. The crystals were filtered off and washed with 2-propanol and diethyl ether. Anal. Found (calc.) for 15 C₁₆H₂₄N₂MoS₄: C 41.00 (41.29), H 5.07 (5.17), N 5.83 (5.98), S 26.98 (27.37), MoS₄ 47.76 (47.84) %

Compound 16 was prepared using similar synthetic procedure. Here instead of (NH₄)₂[MoS₄], (NH₄)₂[WS₄] (348 mg in 10 ml of water) was treated with (R)(+)-α-methylbenzylamine (0.4 ml). Yield (210 mg). Anal. Found (calc.) for 16 C₁₆H₂₄N₂WS₄: C 34.74 (34.53), H 4.27 (4.36), N 5.65 (5.03), S 23.56 (23.05) WS₄ 56.01 (56.08) %.

(NH₄)₂[MoS₄] (260 mg) was dissolved in water (12 ml) containing few drops of ammonia, filtered and to the red coloured solution, (S)(-)-α-methylbenzylamine (0.4 ml) was added. This resulted in the immediate separation of compound 17 (200 mg). The polycrystalline material was filtered, washed with 2-propanol (15 ml) and diethyl ether (15 ml). The filtrate was left aside for crystallization. After a week, needle shaped crystals of compound 17 (100 mg) suitable for single crystal work were obtained. Anal. Found (calc.) for 17 C₁₆H₂₄N₂MoS₄: C 41.71 (41.29), H 5.07 (5.17), N 6.83 (5.98), S 25.95 (27.37), MoS₄ 47.90 (47.84) %

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Compound 18 was prepared using similar synthetic procedure. Here instead of \((\text{NH}_4)_2[\text{MoS}_4]\), \((\text{NH}_4)_2[\text{WS}_4]\) (348 mg, dissolved in 10 ml of water) was treated with \((R)(+)-\alpha\text{-methylbenzylamine} (0.4 \text{ ml})\). Yield (210 mg). Anal. Found (calc.) for 18 \(\text{C}_{16}\text{H}_{24}\text{N}_2\text{WS}_4\): C 34.82 (34.53), H 4.36 (4.36), N 5.68 (5.03), S 23.98 (23.05) WS\(_4\) 56.17 (56.08) %.

Compound 15, 16, 17 and 18 have good stability in air, soluble in water, ammonia, DMSO, DMF, CH\(_3\)CN and insoluble in, CH\(_2\)Cl\(_2\), toluene, alcohol etc.

2.2.10 Preparation of R,S-[PhCH(CH\(_3\))NH\(_3\)]\(_2[\text{MoS}_4]\) 19, R,S-[PhCH(CH\(_3\))NH\(_3\)]\(_2[\text{WS}_4]\) 20

\((\text{NH}_4)_2[\text{MoS}_4]\) (260 mg) was dissolved in water (12 ml) containing few drops of ammonia, filtered and to the red coloured solution, racemic (R,S)-\(\alpha\)-methylbenzylamine (0.4 ml) was added. This resulted in the immediate separation of compound 19 (180 mg). The polycrystalline material was filtered, washed with 2-propanol (15 ml) and diethyl ether (15 ml). The filtrate was left aside for crystallization. After a week, crystalline compound 19 (120 mg) were obtained which was unsuitable for single crystal study. Anal. Found (calc.) for 19 \(\text{C}_{16}\text{H}_{24}\text{N}_2\text{MoS}_4\): C 41.34 (41.29), H 5.13 (5.17), N 6.33 (5.98), S 26.95 (27.37), MoS\(_4\) 47.40 (47.84) %

Compound 20 was prepared using similar synthetic procedure. Here instead of \((\text{NH}_4)_2[\text{MoS}_4]\), \((\text{NH}_4)_2[\text{WS}_4]\) (348 mg, dissolved in 10 ml of water) was treated with racemic (R,S) -\(\alpha\)-methylbenzylamine (0.4 ml). Yield (210 mg). Anal. Found (calc.) for 20 \(\text{C}_{16}\text{H}_{24}\text{N}_2\text{WS}_4\): C 34.22 (34.53), H 4.46 (4.36), N 5.33 (5.03), S 23.34 (23.05) WS\(_4\) 56.40 (56.08) %.

Both, 19 and 20 are stable in air, slightly soluble in water but freely soluble in ammonia, DMSO, DMF, CH\(_3\)CN and insoluble in, CH\(_2\)Cl\(_2\), toluene, alcohol etc. The crystals obtained by this method were not suitable for X-ray studies.

2.2.11 Preparation of [PhCH\(_2\)NMe\(_3\)]\(_2[\text{MoS}_4]\) 21 and [PhCH\(_2\)NMe\(_3\)]\(_2[\text{WS}_4]\) 22

Freshly prepared \((\text{NH}_4)_2[\text{MoS}_4]\) (1.0413g) was dissolved in 40 ml water and then filtered. To the filtrate, Benzyltrimethylammonium hydroxide (4mL of 40% methanolic solution) was added. This resulted in the immediate separation of compound 21 (1.6g). The polycrystalline material was filtered, washed with 2-propanol (15 ml) and diethyl ether (15 ml). The filtrate was left aside for
crystallization. After a week, crystalline compound 21 (500 mg) were obtained. The cell obtained was too big for the structure determination. Anal. Found. (calc.) for 21 (C_{16}H_{24}N_{2}MoS_{4}): C 45.94 (45.77), H 6.31 (6.16), N 5.23 (5.34), S 24.63 (24.45), MoS_{4} 42.40 (42.73) %.

Compound 22 was prepared using similar synthetic procedure. Here instead of (NH_{4})_{2}[MoS_{4}], (NH_{4})_{2}[WS_{4}] (1.044g, dissolved in 20 ml of water) was treated with Benzyltrimethylammonium hydroxide (4mL of 40% methanolic solution). Yield (1.35g). The cell obtained was too big for the structure determination. Anal. Found (calc.) for 22 (C_{16}H_{24}N_{2}WS_{4}): C 39.11 (39.21), H 5.22 (5.28), N 4.51 (4.57), S 20.93 (20.94), WS_{4} 50.40 (50.95) %.

2.2.12 Preparation of [PhCH₂NEt₃]₂[MoS₄] 23 and [PhCH₂NEt₃]₂[WS₄] 24

Freshly prepared (NH_{4})₂[MoS_{4}] (1.0413g) was dissolved in 40 ml water and then filtered. To the filtrate, Benzyltriethylammonium chloride (2.2738g dissolved in 10ml) was added. This resulted in the immediate separation of compound 23 (1.69g). The polycrystalline material was filtered, washed with 2-propanol (15 ml) and diethyl ether (15 ml). The filtrate was left aside for crystallization. After a week, crystalline compound 21 (580 mg) were obtained. The cell obtained was too big for the structure determination. Anal. Found. (calc.) for 23 (C_{26}H_{44}N_{2}MoS_{4}): C, 51.08 (51.28) H, 7.27 (7.30) N 4.58 (4.60) S 20.95 (21.06), MoS_{4} 36.80 (36.83) %.

Compound 24 was prepared using similar synthetic procedure. Here instead of (NH_{4})₂[MoS_{4}], (NH_{4})₂[WS_{4}] (1.044g, dissolved in 30 ml of water) was treated with Benzyltriethylammonium chloride (2.2738g dissolved in 10ml) was added. Yield (1.3643 g). The cell obtained was too big for the structure determination. Anal. Found (calc.) for 24 (C_{26}H_{44}N_{2}WS_{4}): C 44.56 (44.81), H 6.22 (6.38), N 4.01 (4.02), S 18.35 (18.41), WS_{4} 44.80 (44.79) %.

2.2.13 Preparation of (pipH)₂[MoS₄] 25 and (pipH)₂[WS₄] 26

Anhydrous piperazine (1.6 g) was mixed with (NH_{4})₂[MoS_{4}] (0.520 g) and the solid mixture was mechanically ground in a mortar with a pestle for 5 min. The resulting fine powder was dissolved in water (15 ml) and briefly warmed on a water bath to expel traces of ammonia. The reaction mixture was filtered and the red filtrate was left
aside for crystallization to obtain red needles. The crystalline product was isolated by filtration, washed with 2-propanol, followed by diethyl ether and air dried to yield 0.5044 g of compound 25. Anal. Calc. for C₈H₂₂N₄MoS₄: C 23.95 (24.11), H 5.63 (5.56), N 14.02 (14.06), S 32.55 (32.19), MoS₄ 56.12 (56.26) %.

Compound 26

Anhydrous piperazine (1.162 g) was mixed with (NH₄)₂[WS₄] (0.6965 g) and the solid mixture was mechanically ground in a mortar with a pestle for 5 min. The resulting fine powder was dissolved in water (10 ml) and briefly warmed on a water bath to expel traces of ammonia. The reaction mixture was filtered and the yellow filtrate was left aside for crystallization to obtain yellow needles. The crystalline product was isolated by filtration, washed with 2-propanol, followed by diethyl ether and air dried to yield 0.50 g of compound 26. Anal. Found (calc.) for C₈H₂₂N₄WS₄: C 19.79 (19.75), H 4.56 (4.57), N 11.55 (11.52), S 27.26 (26.37), WS₄ 64.31 (64.16) %.

Both 25 and 26 are stable in air, freely soluble in water, ammonia, DMSO, DMF and insoluble in CH₃CN, CH₂Cl₂, toluene, alcohol etc.

2.2.14 Preparation of dienH₂[MoS₄] 29 and dienH₂[WS₄] 30 (form 1)

260 mg of (NH₄)₂[MoS₄] was dissolved in water (15 ml) and into this added 0.2 ml of diethylenetriamine (dien). After a week, marron red needles were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (10 ml) followed by diethyl ether (10 ml), and dried under vacuum. Yield (0.26 g). Anal. Found (calc.) for C₄H₁₅N₃MoS₄: C 14.50 (14.58), H 4.99 (4.60), N 12.66 (12.76), S 39.03 (38.94), MoS₄ 68.27 (68.06) %.

Compound 30 was prepared by mixing aqueous solutions of (NH₄)₂[WS₄] (348 mg, dissolved in 10 ml water) and 0.3 ml of dien. After a week, yellow needles were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (10 ml) followed by diethyl ether (10 ml), and dried under vacuum. Yield (0.26 g). Anal. Found (calc.) for C₄H₁₅N₃WS₄: C 11.48 (11.51), H 3.66 (3.63), N 10.86 (10.97), S 30.65 (30.74), WS₄ 74.92 (74.79) %.
2.2.15 Preparation of dienH$_2$[MoS$_4$] $^{31}$ and dienH$_2$[WS$_4$] $^{32}$ (form 2)

1.3016 g of (NH$_4$)$_2$[MoS$_4$] was dissolved in water (30 ml) and into this added 1.5 ml of diethylenetriamine (dien). After a week, marron red blocks were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (10 ml) followed by diethyl ether (10 ml), and dried under vacuum. Yield (0.8 g). Anal. Found (calc.) for $^{31}$ C$_4$H$_{15}$N$_3$MoS$_4$: C 14.54 (14.58), H 4.69 (4.60), N 12.76 (12.76), S 38.83 (38.94), MoS$_4$ 68.13 (68.06) %.

Compound $^{32}$ was prepared by mixing aqueous solutions of (NH$_4$)$_2$[WS$_4$] (1.3929 g, dissolved in 30 ml water) and 1.5 ml of dien. After a week, yellow blocks were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (10 ml) followed by diethyl ether (10 ml), and dried under vacuum. Yield (0.7 g). Anal. Found (calc.) for $^{32}$ C$_4$H$_{15}$N$_3$WS$_4$: C 11.58 (11.51), H 3.60 (3.0), N 10.96 (10.97), S 30.75 (30.74), WS$_4$ 74.82 (74.79) %.

2.2.16 Preparation of [N-ethylpипH$_2$][MoS$_4$] $^{33}$ and [N-ethylpипH$_2$][WS$_4$] $^{34}$

Molybdic acid (2 g) was dissolved in a mixture of N-ethyl piperazine (10 ml) and distilled water (15 ml). A rapid stream of H$_2$S gas was bubbled into this for 30 min at 60 °C, resulting in the formation of a red solid. The crystals were isolated by filtration, washed with isopropyl alcohol (20 ml) followed by diethyl ether (20 ml), and dried under vacuum. Yield (2.0 g). Anal. Found (calc.) for $^{33}$ C$_6$H$_{16}$N$_2$MoS$_4$: C 21.54 (21.17), H 4.69 (4.75), N 8.76 (8.23), S 38.03 (37.68), MoS$_4$ 65.13 (65.86) %.

Compound $^{34}$

348 mg of (NH$_4$)$_2$[WS$_4$] was dissolved in water (15 ml) and into this added 0.4 ml of N-ethylpiperazine. After a week, yellow crystals were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (10 ml) followed by diethyl ether (10 ml), and dried under vacuum. Yield (0.26 g). Anal. Found (calc.) for $^{34}$ C$_6$H$_{16}$N$_2$WS$_4$: C 16.80 (16.82), H 3.70 (3.77), N 6.47 (6.54), S 30.05 (29.95), WS$_4$ 72.82 (72.87) %.

2.2.17 Preparation of [N-methylpипH$_2$][MoS$_4$] · $\frac{1}{2}$H$_2$O $^{35}$ and [N-methylpипH$_2$][WS$_4$] · $\frac{1}{2}$H$_2$O $^{36}$

Molybdic acid (2 g) was dissolved in a mixture of N-methyl piperazine (6 ml) and distilled water (20 ml). A rapid stream of H$_2$S gas was bubbled into this for 30
min at 60 °C. The red blocks (0.8 g) were obtained next day. The crystals were isolated by filtration, washed with isopropyl alcohol (20 ml) followed by diethyl ether (20 ml), and dried under vacuum. Anal. Found (calc.) for \( \text{C}_5\text{H}_{15}\text{N}_2\text{O}_{0.5}\text{MoS}_4 \): C 17.93 (17.90), H 4.59 (4.52), N 8.36 (8.35), S 38.21 (30.24), MoS\(_4\) 58.95 (58.84) %.

**Compound 36**

1.34g of \((\text{N}_1\text{I}4)_2[\text{WS}_4]\) was dissolved in water (20 ml) and into this added 0.7ml of N-methylpiperazine. After a week, orange-yellow crystals were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (10 ml) followed by diethyl ether (10 ml), and dried under vacuum. Yield (0.67 g). Anal. Found (calc.) for \( \text{C}_5\text{H}_{15}\text{N}_2\text{O}\text{.5WS}_4 \): C 14.80 (14.18), H 3.50 (3.58), N 6.67 (6.62), S 30.25 (30.30), WS\(_4\) 73.82 (73.73) %.

### 2.2.18 Preparation of \([\text{N-methylpipH}_2][\text{MoS}_4] \cdot \text{H}_2\text{O}\) 37

and \([\text{N-methylpipH}_2][\text{WS}_4] \cdot \text{H}_2\text{O}\) 38

Molybdic acid (3 g) was dissolved in a mixture of N-methyl piperazine (8 ml) and distilled water (30 ml). A rapid stream of H\(_2\)S gas was bubbled into this for 30 min at 60 °C. The red needle shaped crystals were isolated by filtration, washed with isopropyl alcohol (20 ml) followed by diethyl ether (20 ml), and dried under vacuum. Yield 2.0g. Anal. Found (calc.) for \( \text{C}_5\text{H}_{16}\text{N}_2\text{OMoS}_4 \): C 17.53 (17.43), H 4.68 (4.69), N 8.16 (8.13), S 37.21 (37.24), MoS\(_4\) 64.95 (65.09) %.

**Compound 38**

348mg of \((\text{NH}_4)_2[\text{WS}_4]\) was dissolved in water (15 ml) and into this added 0.7ml of N-methylpiperazine. After a week, yellow crystals were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (10 ml) followed by diethyl ether (10 ml), and dried under vacuum. Yield (0.2 g). Anal. Found (calc.) for \( \text{C}_5\text{H}_{16}\text{N}_2\text{OWS}_4 \): C 13.80 (13.89), H 3.65 (3.74), N 6.47 (6.48), S 29.65 (29.67), WS\(_4\) 72.82 (72.19) %.

### 2.2.19 Preparation of \((2\text{-pipH-1-EtNH}_3)[\text{WS}_4] \cdot \frac{1}{2}\text{H}_2\text{O}\) 39

348mg of \((\text{NH}_4)_2[\text{WS}_4]\) was dissolved in water (20 ml) and into this added aqueous solution of 2-piperazine-1-ethylamine \((2\text{-pipH-1-EtNH}_2)\) (0.4mL of amine
dissolved in 2ml water). After a week, yellow crystals were formed. The crystals were isolated by filtration, washed with isopropyl alcohol (10 ml) followed by diethyl ether (10 ml), and dried under vacuum. Yield (0.22 g). The crystals obtained by this method were suitable for X-ray studies. Anal. Found (calc.) for \( \text{C}_6\text{H}_{18}\text{N}_3\text{O}_{3.5}\text{W}_4 \): C 15.85 (15.93), H 4.15 (4.02), N 9.27 (9.29), S 28.45 (28.36), WS\(_4\) 69.12 (69.00) %

### 2.2.20 Preparation of \((\text{NH}_4)(\text{Dabcoll})\text{W}_4\) 40

To an aqueous solution of \((\text{NH}_4)_2\text{[W}_4\text{]} \) (348 mg, 1 mmol in 10 ml of water), Diazabicyclooctane (Dabco) (0.16g dissolved in 5ml of water) was added and the mixture was left undisturbed for crystallization. After a week, yellow crystals formed were isolated by filtration, washed with cold water, followed by isopropyl alcohol (10 ml) and diethyl ether (10 ml). The compound was dried in air. Yield (0.1984g). The crystals are stable in air, soluble in water, freely soluble in ammonia, DMSO, DMF and insoluble in CH\(_3\)CN, CH\(_2\)Cl\(_2\), toluene, alcohol etc. Anal. Found (calc.) for \( \text{C}_6\text{H}_{16}\text{N}_3\text{W}_4 \): C 16.38 (16.29), H 3.49 (3.65), N 9.48 (9.50), S 29.15 (29.00) %

### 2.3 Synthetic procedures for oxido-trisulfidotungstate

**a. Synthesis of \((\text{NH}_4)_2\text{[W}_3\text{OS}_3\text{]} \)**

\( \text{H}_2\text{WO}_4 \) (5.09 g) was dissolved in a mixture of concentrated ammonia (20 ml) and water (5 ml) and the solution was filtered. Hydrogen sulfide gas was bubbled rapidly into the solution for 15 min at ambient temperature causing the precipitation of a minimal amount of \([\text{NH}_4]_2[\text{WO}_2\text{S}_2]\). The reaction mixture was filtered into ice-cold isopropyl alcohol (500 ml) and the product separated as a yellow solid which was isolated by filtration, washed with isopropyl alcohol and diethylether and dried in vacuo. Yield (5.1 g). Anal. Found (calc.) for \( \text{H}_8\text{N}_2\text{W}_3\text{OS}_3 \): H 2.30 (2.40); N 8.38 (8.43)

**2.3.1 Preparation of en\(\text{H}_2\text{[W}_3\text{OS}_3\text{]} \)** 41

\((\text{NH}_4)_2\text{[W}_3\text{OS}_3\text{]} \) (664mg) was dissolved in 10 ml of distilled water and to this 0.3 ml of ethylenediamine (en) was added in drops. The solution was left undisturbed for crystallization. After 1-2 days, yellow crystals were isolated by filtration, washed with ice cold water (5 ml) followed by isopropyl alcohol (10 ml) and diethyl ether (10
ml). The compound was dried in air. Yield (500 mg). Anal. Found (calc.) for \( \text{C}_2\text{H}_{10}\text{N}_2\text{O}_2\text{WS}_4 \): C 6.61 (6.71), H 2.85 (2.82), N 7.80 (7.82), S 26.88 (26.86) %.

2.4 Synthesis of organic ammonium salts of oxidometalate

2.4.1. Preparation of \((\text{pipH}_2)[\text{CrO}_4]\) \(^{41}\)

Ammonium chromate (1.52 g) was dissolved in water (5 ml) and mixed with an aqueous solution of piperazine (0.86 g, dissolved in 4 ml of water). The yellow coloured solution thus obtained was filtered and kept for crystallization. After 2 days, yellow block-like crystals were obtained. The crystalline product was filtered and washed with ice-cold water (−5 ml) and air-dried. Yield (1.4 g). The crystals obtained were suitable for X-ray structure determination. The compound is stable in air, soluble in water, ammonia, DMSO, DMF etc. Anal. Found (calc.) for \( \text{C}_4\text{H}_{12}\text{N}_2\text{O}_4\text{Cr} \): C 23.50 (23.53), H 5.85 (5.94), N 13.70 (13.72), Cr 25.41 (25.47) %.

2.4.2. Preparation of \((\text{pipH}_2)[\text{Cr}_2\text{O}_7]\) \(^{42}\)

\((\text{NH}_4)_2[\text{Cr}_2\text{O}_7]\) (1.512 g) was dissolved in distilled water (10 ml) containing 0.3 ml of concentrated \( \text{H}_2\text{SO}_4 \) and this solution was slowly added to a solution of piperazine hexahydrate (1.2 g) dissolved in water (4 ml), resulting in the formation of yellow-orange crystalline blocks of the title complex. The crystals were filtered off, washed with ice-cold water (1 ml) and dried in air. Yield (1.62 g). The crystals are quite stable in air. Anal. Found (calc.) for \( \text{C}_4\text{H}_{12}\text{N}_2\text{O}_7\text{Cr}_2 \): C 15.17 (15.79), H 4.11 (3.98), N 9.39 (9.21) %.

2.4.3. Preparation of \([\text{Ni(en)}_3][\text{CrO}_4]\) \(^{43}\)

\( \text{K}_2[\text{CrO}_4] \) (194 mg) was dissolved in water (15 ml) and \([\text{Ni(en)}_3]\text{Cl}_2\cdot2\text{H}_2\text{O} \) (345 mg dissolved in 25 ml in water) was slowly added at room temperature. After few days crystals were obtained. The crystalline product was filtered and washed with ice-cold water (−5 ml) and air-dried. Yield (213 mg). The crystals obtained were not suitable for structure determination.
2.4.3. Preparation of [Ni(en)$_3$][Cr$_2$O$_7$] 45

K$_2$[Cr$_2$O$_7$] (294 mg) was dissolved in water (25 ml) and [Ni(en)$_3$]Cl$_2$.2H$_2$O (345 mg dissolved in 25 ml in water) was slowly added at room temperature. After a week crystals were obtained. The crystalline product was filtered and washed with ice-cold water (~5 ml) and air-dried. Yield (270mg). The crystals obtained were suitable for structure determination.

2.4.4. Preparation of [n-C$_4$H$_9$NH$_3$]$_8$ [Mo$_7$O$_{24}$][MoO$_4$].3H$_2$O 46

Molybdic acid (3.24 g) was dissolved in a mixture of n-butylamine (5 ml) and distilled water (5 ml). After few days crystals were obtained. The crystalline product was filtered and air-dried. Yield (2.67g). The crystals obtained were suitable for structure determination.

2.4.5. Photochemical reaction of [n-C$_4$H$_9$NH$_3$]$_8$ [Mo$_7$O$_{24}$][MoO$_4$].3H$_2$O

[n-C$_4$H$_9$NH$_3$]$_8$ [Mo$_7$O$_{24}$][MoO$_4$].3H$_2$O (1.2 g) was dissolved in distilled water (4 ml) and exposed to sunlight for 30 minutes resulted in an intense blue colored solution. This solution was kept for crystallization and the blue crystals (compound 47) were obtained. The crystalline product was filtered and air-dried. Yield (0.610g). The crystals obtained were suitable for structure determination.

2.4.6. Preparation of [n-C$_4$H$_9$NH$_3$]$_6$ [Mo$_7$O$_{24}$].4H$_2$O 48

[n-C$_4$H$_9$NH$_3$]$_8$ [Mo$_7$O$_{24}$][MoO$_4$].3H$_2$O (1.2 g) was dissolved in distilled water (4 ml) and the solution was kept for crystallization resulted in the formation of compound 48 after few days. The crystalline product was filtered and air-dried. Yield (0.910 g). The crystals obtained were suitable for structure determination.

2.5 Synthesis of organic ammonium salts of thiosulfate

2.5.1 Preparation of enH$_2$[S$_2$O$_3$] 49

To an aqueous solution of (NH$_4$)$_2$(S$_2$O$_3$) (5.93 g) in water (10 ml) was added 2.68ml of ethylenediamine (en). The reaction mixture was filtered and the clear filtrate was heated on the water bath for ~ 15 min to expel ammonia gas. The reaction mixture was filtered and left undisturbed. After a week, colourless blocks were...
obtained from the reaction mixture. The crystals were filtered, washed with a little ice-cold water and dried in air. Yield 6.0 g.

2.5.2 Preparation of [pipH₂][S₂O₃] · H₂O 50

To an aqueous solution of (NH₄)₂(S₂O₃) (5.93 g) in water (10 ml) was added a solution of piperazine (3.44 g) in water (10 ml). The reaction mixture was filtered and the clear filtrate was heated on the water bath for ~ 15 min to expel ammonia gas. The reaction mixture was filtered and left undisturbed. After a week, colourless blocks were obtained from the reaction mixture. The crystals were filtered, washed with a little ice-cold water and dried in air. Yield 6.1 g.

Anal. Calc. for C₄H₁₄N₂O₄S₂ (218.29): C, 22.00; H, 6.48; N, 12.83 S, 29.37 Found: C, 22.00; H, 6.51, N, 13.25; S 30.34.

2.6 Reactivity Studies

**Re-investigation of (NH₄)₆[Mo₇S₂₄] 51**

2.6.1 Preparation of compound 51 [158]

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, H₂S gas was continuously passed for 5 h and the temperature was maintained at 60°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°C. The solid was isolated by filtration, washed well with isopropyl alcohol, followed by diethyl ether and dried in vacuo. Yield 4.3 g. It is to be noted that after half an hour crystals of (NH₄)₂[MoS₄] started appearing in the solution. These crystals tend to block the passage of H₂S gas. Hence it is desirable to use a wide-mouthed gas-passing tube or alternatively change the tube periodically. Anal. Found (Calcd) for (NH₄)₆[Mo₇S₂₄]: (NH₄)13.84 (6.98), Mo 36.70 (43.34) S 49.08 (49.68) %.

IR: ν (Mo─S) 478 cm⁻¹; UV-Vis (dil. NH₄OH): 469, 317 and 242 nm.
2.6.2 Reactions of \((\text{NH}_4)_2[\text{MoS}_4]\) and compound 51 with sodium tetraphenylborate

\((\text{NH}_4)_2[\text{MoS}_4]\) (130 mg) was dissolved in water (10 ml). A solution of (360 mg) of sodium tetraphenylborate (NaBPh₄) in water (30 ml) was slowly added in drops into this solution of \((\text{NH}_4)_2[\text{MoS}_4]\) under stirring. This resulted in the immediate precipitation of \(\text{NH}_4(\text{BPh}_4)\). The reaction mixture was kept aside for 1 h and filtered. The white precipitate of \(\text{NH}_4(\text{BPh}_4)\) was washed well with ice-cold water till the washings were colourless, and then dried in vacuum and weighed to get 340 mg of precipitate. %\(\text{NH}_4\) 13.85%.

In another experiment, the reaction of 130 mg of \((\text{NH}_4)_6[\text{Mo}_7\text{S}_{24}]\) with (360 mg) of \([\text{NaBPh}_4]\) in water (30 ml) under identical conditions as mentioned above resulted in the formation of 336 mg of \(\text{NH}_4(\text{BPh}_4)\). %\(\text{NH}_4\) 13.84%.

**Note:** The analytical data are not in agreement with the proposed formula \((\text{NH}_4)_6[\text{Mo}_7\text{S}_{24}]\) [158] but to \((\text{NH}_4)_2[\text{MoS}_4]\) [159].

2.6.3 Reaction of \((\text{NH}_4)_2[\text{MS}_4]\) with \([\text{PhCH}_2\text{N(C}_2\text{H}_5)_3]\text{Cl}\)

The reaction of an aqueous solution of \((\text{NH}_4)_2[\text{MoS}_4]\) (3.2 g in 30 ml water) with aqueous \([\text{PhCH}_2\text{N(C}_2\text{H}_5)_3]\text{Cl}\) (2.733 g dissolved in 20 ml of \(\text{H}_2\text{O}\)) solution under constant stirring for about 1 h resulted in the formation of \([\text{PhCH}_2\text{N(C}_2\text{H}_5)_3]_2[\text{MoS}_4]\). Yield (5.5 g, 73 % based on Mo). Anal. Found (calc.) for \(\text{C}_{26}\text{H}_{44}\text{N}_2\text{MoS}_4\): C 51.08 (51.28), H 7.27 (7.30), N 4.58 (4.60), S 20.95 (21.06), Mo 15.67 (15.75), \(\text{MoS}_4\) 36.62 (36.82), \(\text{MoO}_3\) 22.23 (23.64) %, decomposition temp 130°C, DSC onset temperature 130 °C.

\[
2 \left[\text{PhCH}_2\text{N(C}_2\text{H}_5)_3\right]\text{Cl} + (\text{NH}_4)_2[\text{MoS}_4]^{2-} \rightarrow \left[\text{PhCH}_2\text{N(C}_2\text{H}_5)_3\right]_2[\text{MoS}_4] + 2 \text{NH}_4\text{Cl}
\]

2.6.4 Reaction of \((\text{NH}_4)_2[\text{MoS}_4]\) with \([\text{Ni(en)}_3]\text{Cl}_2\cdot2\text{H}_2\text{O}\)

To an aqueous ammoniacal solution of \((\text{NH}_4)_2[\text{MoS}_4]\) (260 mg in 15 ml \(\text{H}_2\text{O}\) containing \(\text{NH}_3\)), \([\text{Ni(en)}_3]\text{Cl}_2\cdot2\text{H}_2\text{O}\) (370 mg in 20 ml in \(\text{H}_2\text{O}\)) was added which resulted in the formation of the previously reported \([\text{Ni(en)}_3][\text{MoS}_4]\). The reaction mixture was kept aside for 1 h and filtered. The orange red polycrystalline compound
was washed well with cold water till the washings were colorless and dried in vacuum and weighed to get 460 mg of product.


2.6.5 Reaction of [(PhCH₂N(C₂H₅)₃)₂[MoS₄] with [Ni(en)₃]Cl₂·2H₂O

[(PhCH₂N(C₂H₅)₃)₂[MoS₄] (609 mg) was dissolved in 20 ml of CH₃CN and slowly added in drops to an aqueous solution of [Ni(en)₃]Cl₂·2H₂O (370 mg in 20 ml) under stirring. The reaction mixture was kept aside for 1 h and filtered. The orange red polycrystalline [Ni(en)₃][MoS₄] was washed with cold water till the washings were colorless and dried in vacuum and weighed to get 460 mg of compound.