SYNOPSIS

The thesis entitled, "Organic Ammonium Salts of Group VI Oxometalates and Thiometalates: Synthesis, Spectroscopic, Thermal, X-ray Structure and Reactivity Studies" consists of five chapters as depicted in Scheme I. The first chapter reviews the work carried out by various researchers in this field and highlights of the known work are presented. The second chapter deals with scope of the present investigation. The details of experimental work, which include synthesis and reactivity studies, are discussed in the Chapter 3. The characterisation of synthesised complexes by various analytical techniques is described in the fourth chapter. The final chapter summarizes the present work and the thesis ends with some recommendations for future work.

The first chapter reviews the known chemistry of M-X complexes (M= Mo, W and Cr, X= S, O). The elements of group VI (Mo and W) are essential trace elements for many organisms, including human beings and animals. Molybdenum is required for almost all molybdenum enzymes containing sulfur atoms [1]. Many sulfur-bridged compounds of tungsten, a congener of molybdenum, are also known. Molybdenum is also present as the Fe/Mo cofactor of nitrogenase [2] and oxidoreductase enzymes [3]. The sulfur complexes of group VI metals Mo [4] and W [5] are a unique class of...
compounds encompassing an unusually wide range of metal-sulfur stoichiometry, metal oxidation states, coordination geometries and different bonding modes of sulfido ligands. The structural diversity exhibited by Mo/W-S complexes can be evidenced from the structural characterisation of a variety of Mo/W-S complexes and this is an important reason for the continuing research in this rapidly growing field.

The Mo-S complexes \([\text{MoS(S}_4^2\text{)}_2]^2^-\), \([\text{Mo}_2\text{(S)}_2(\mu-\text{S})_2\text{(S}_4\text{)}_2]^2^-\), \([\text{Mo}_2\text{(S)}_2(\mu-\text{S})_2\text{(S}_4\text{)}_2]^2^-\), \([\text{SMo(MoS}_4\text{)}_2]^2^-\) etc. which can be prepared from \([\text{MoS}_4]^2^-\) by reacting with the appropriate reagents, serve as a few examples, to illustrate the structural diversity encountered in Mo-S chemistry [6-10]. It is well documented that the \([\text{MoS}_4]^2^-\) ion can behave like a bidentate ligand to form sulphur bridged multi-metal complexes [11,12]. Like \([\text{MoS}_4]^2^-\), \([\text{WS}_4]^2^-\) has been used as a reagent for the synthesis of several structurally diverse W-S complexes such as \([\text{W}_2\text{(S}_2\text{)}_2(\mu-\text{S})_2\text{(S}_4\text{)}_2]^2^-\) [9], \([\text{W}_2\text{(S)}_2(\mu-\text{S})(\eta^2-\text{S}_2\text{)}_4]^2^-\) [13], \([\text{W}_2\text{(S)}_2(\mu-\text{S})(\mu-\text{η}^3-\text{S}_2)(\eta^2-\text{S}_2\text{)})_4]^1\) [14], \([\text{W(WS}_4\text{)}_2]^2^-\) [15], \([\text{SW(WS}_4\text{)}_2]^2^-\), \([\text{W}_3\text{S}_{10}]^2^-\) [16], \([\text{(W}_2\text{S}_4)(\text{WS}_4\text{)}_2]^2^-\) [17]. Although the ammonium salts of tetrathiometalates of the group VI metals (NH$_4$)$_2$[M$_4$] (M = Mo, W) were first investigated by Berzelius [18,19] in the beginning of the nineteenth century, much of its chemistry has been developed only in the last three decades primarily by Müller and coworkers [11].

In recent years, the chemistry of soluble metal sulfide complexes is emerging as a frontier area of research in view of the relevance of metal sulfide compounds in hydrosulfurisation (HDS), hydrodeoxygenation (HDO), hydrodenitrogenation (HDN) and hydrometallation (HDM), and application in energy, environmental, and material science [20]. The use of organic ammonium tetrathiomolybdates and tetrathiotungstestes as precursor materials for the preparation of highly dispersed MoS$_2$ and WS$_2$ catalysts respectively is showing much promise in the field of hydrodesulfurisation (HDS) catalysis [21]. It has also been reported that the chemical properties of \([\text{MoS}_4]^2^-\) can be substantially changed by surrounding it with organic ammonium cations for example cetyltriethylammonium [22]. The synthesis and HDS activity of Ni-Mo-S [23] and Co-Mo-S catalyst [24] both derived from thiomolybdates have been reported recently.

The use of thiomolybdate as a versatile reagent for the preparation of a variety of compounds and also its relevance in bioinorganic chemistry and medicine has been
reviewed [25]. In recent years the use of tetrathiomolybdate for the treatment of metastatic cancer has added an entire new dimension to its chemistry [26,27]. Recently the reactivity characteristics of [MoS$_4$]$^{2-}$ towards trialkyl phosphine like PMe$_3$ (Me is methyl) have been reported emphasizing the role of proton sources for S transfer [28]. A possible reason for the differing reactivity of (NH$_4$)$_2$[MoS$_4$] and (Et$_4$N)$_2$[MoS$_4$] has been attributed to short H-bonding contacts between the cation and anion in (NH$_4$)$_2$[MoS$_4$] [28], a structural feature which is absent in (Et$_4$N)$_2$[MoS$_4$] [29]. The use of Mo-S complexes like (NH$_4$)$_2$[Mo$_2$S$_2$]$_2$ [30], (C$_5$H$_{12}$N)$_2$[MoS$_4$] [31], [(PhCH$_2$)N(C$_2$H$_5$)$_3$]$_2$[MoS$_4$] [32,33], (NH$_4$)$_2$[MoS$_4$] [34,35] as sulfur transfer reagents in organic syntheses, for the preparation of organo-sulfur compounds has added an extra dimension to the known Mo-S compounds. It has recently been shown by Bensch and coworkers that phase pure sulfido complexes of Mo and W like [Ni(en)$_3$][MoS$_4$] (en is ethylenediamine) [36], [Ni(en)$_3$][WS$_4$] [37], [Co$_2$(tren)$_3$][MoS$_4$]$_2$ [38], [Ni(tren)$_2$][WS$_4$] (tren is tris(2-aminoethylamine)) [39] and [Mn(dien)$_2$][MoS$_4$] (dien is diethylenetriamine) [40] can be prepared under mild solvothermal conditions. In this context, the study of the reactivity characteristics of [MS$_4$]$^{2-}$ complexes with different organic bases like en and other related amines can be useful to understand the influence of the chemical and geometrical properties of the solvent on the product formation.

The second chapter outlines the scope of the present work. A primary aim of the present investigation is to develop simple synthetic strategies for the convenient synthesis of newer organic ammonium tetrathiomolybdates and tetrathiotungstates using readily available starting materials. It may be noted that several reported extended network systems derived from [MoS$_4$]$^{2-}$ and [WS$_4$]$^{2-}$ have been assembled under solvothermal conditions. It is of interest to develop synthetic methods for the construction of M-S complexes under ambient conditions. In this context two different synthetic methods along with the previously used simple cation exchange method, are used for the syntheses of a variety organic ammonium tetrathiometalates. The use of organic amines with differing H-bonding donors and steric factors can lead to the formation of structurally different extended network compounds. Hence various organic amines with different steric factors and different number of potential H-bonding donors have been chosen in this work. The different organic amines used in this work are depicted in Scheme II.
The third chapter describes the full details of the experimental aspects of the present work, which includes the synthesis of organic ammonium tetrathiometalates, oxochromates as well as their reactivity studies. The reaction sequences employed for the synthesis are summarized in Scheme III. Scheme IV summarizes the reactivity studies of the synthesized complexes. As a part of reactivity study of tetrathimolybdates and tetra-thiotungstates, a convenient method has been developed for the quantitative estimation of \([MS_4]^{2-}\) core. Here aqueous or organic solution of \([MS_4]^{2-}\) complexes was reacted with \([Ni(en)_3]^{2+}\) solution which results in formation of highly insoluble \([Ni(en)_3][MS_4]\) (M= Mo, W). This method has been used to correctly formulate the earlier reported ammonium tetracosathioheptamolybdate as ammonium tetrathiomolybdate [41].

The synthetic aspects and physicochemical as well the structural investigations of newly synthesized complexes are described in fourth chapter. The complexes synthesized in the present work have been studied by a variety of methods (Scheme V) and the details of these investigations are elaborated in this chapter. The formation of the organic ammonium tetrathiometalates has been achieved by using different synthetic routes as shown in Scheme III. The syntheses of ammonium salts of \([MS_4]^{2-}\) (M = Mo, W) are known from the days of Berzelius. This method (reaction 1) involves passing a rapid stream of \(H_2S\) gas into an aqueous ammoniacal solution of heptamolybdate (in case of Mo) or tungstic acid (in case of W) which results in the formation of well known \((NH_4)_2[MoS_4]\) or \((NH_4)_2[WS_4]\) complexes. This method has been slightly modified in the present work (method A) (reaction 2) and an organic amine has been used instead of ammonia.

\[
[Mo_7O_{24}]^{6-} \text{ or } [MO_4]^{2-} + H_2O + NH_3 \xrightarrow{H_2S} (NH_4)_2[MS_4] \quad ... \quad 1
\]

\[
[Mo_7O_{24}]^{6-} \text{ or } [MO_4]^{2-} + \text{organic amine} \xrightarrow{H_2S} \text{organic ammonium}[MS_4] \quad ... \quad 2
\]
NH₂-CH₂-CH₂-NH₂  
1,3-pn

(CH₃)₂N-(CH₂)₂-N(CH₃)₂  
tmen

N(CH₂-CH₂-NH₂)₃  
tren

NH₂-(CH₂)₂-NH-(CH₂)₂-NH₂  
dipn

NH₂-(CH₂)₂-CH₂-NH-CH₃  
N-Meen

[NH₂-(CH₂)₂-NH-(CH₂)₂-NH-(CH₂)₂-NH₂  
trien

[Ph-CH₂-N(CH₃)₂-(CH₂)₂-N(CH₂)₂-Ph]Br₂.2H₂O  
dbtBr₂.2H₂O

\[
\begin{align*}
\text{pip} & \quad \text{dabco} \\
\text{1, 4-dmpip} & \\
\text{NH₂-NH₂} & \\
\text{hydrazine} & \\
\text{trans(±)1,2-diaminocyclohexane} & \text{trans 1,4-diaminocyclohexane}
\end{align*}
\]

Scheme II
Scheme III

Scheme IV

Method A = Modified Berzelius Method
Method B = Base promoted Cation Exchange
Method C = Simple cation exchange
The organic ammonium tetrathiometalate complexes can also be prepared by base promoted cation exchange method (method B) where in a weak base like NH$_3$ of (NH$_4$)$_2$[MS$_4$] is replaced by stronger base organic amine. The base promoted cation exchange method can be shown as follows (reaction 3).

$$(\text{NH}_4)_2[\text{MS}_4] + \text{organic amine} \rightarrow \text{organic ammonium}[\text{MS}_4] + 2 \text{NH}_3 \ldots 3$$

The base promoted cation exchange method has been shown to be a convenient as well as general method for the high yield synthesis of organic ammonium tetrathiometalates. (trenH$_2$)[MS$_4$]H$_2$O (M= Mo, W) (tren is tris(2-aminooctyl)amine) complexes are the first examples of structurally characterized hydrated organic diammonium tetrathiometalates obtained by this method.
Two highly insoluble organic ammonium tetrathiometallate complexes namely (dbt)[MoS₄] and (dbt)[WS₄] have been synthesized by simple cation exchange method (method C) where in aqueous ammoniacal solution of (NH₄)₂[MS₄] was reacted with aqueous solution dbtB₂.2H₂O (dbt is N,N'-dibenzyl-N,N,N'-tetramethylethylene-diammonium) as shown in below equation 4.

\[(\text{NH}_4)_2[\text{MS}_4] + (\text{dbt})\text{Br}_2 \cdot 2\text{H}_2\text{O} \rightarrow (\text{dbt})[\text{MS}_4] + 2 \text{NH}_4\text{Br} + 2 \text{H}_2\text{O} \quad \text{(M = Mo, W)}\]

The chemistry of thiometalates has been extended to the corresponding oxochromates and this work has resulted in the isolation of two organicdiammonium oxochromate salts namely ethylenediammonium chromate (enH₂)[CrO₄] and ethylenediammonium-dichromate (enH₂)[Cr₂O₇] (equation 5 and 6).

\[(\text{NH}_4)_2[\text{CrO}_4] + (\text{enH}_2)\text{Cl}_2 \rightarrow (\text{enH}_2)[\text{CrO}_4] + 2 \text{NH}_4\text{Cl} \quad \text{... 5}\]

\[(\text{NH}_4)_2[\text{Cr}_2\text{O}_7] + (\text{enH}_2)\text{Cl}_2 \rightarrow (\text{enH}_2)[\text{Cr}_2\text{O}_7] + 2 \text{NH}_4\text{Cl} \quad \text{... 6}\]

A combination of UV-Vis, IR, Raman and NMR spectroscopic techniques has been used for the characterisation of new complexes investigated in this work. The UV-Visible spectra of tetrathimolybdate and tetrathiottungstate complexes exhibit characteristic bands due to charge transfer transitions of tetrahedral [MoS₄]²⁻ and [WS₄]²⁻ moieties respectively. IR and Raman spectra of almost all new complexes synthesised in this work show splitting of M-S vibration. The maximum splitting of Mo-S and W-S bands are observed in the IR spectra of (pipH₂)[MoS₄] and (pipH₂)[WS₄] complexes respectively which can be attributed to differing degree of distortion of the [MS₄] tetrahedron. The splitting of M-S bands in these complexes is further revealed from the crystal structure determination as evidenced by short and long M-S bond lengths.

The newer organic ammonium tetrathiometalates prepared in this work has also been studied by thermoanalytical techniques. The final residue obtained after thermal decomposition of these complexes was characterized by elemental analysis, X-ray powder pattern and ESEM–EDAX studies. On heating at higher temperatures, organic
ammonium tetrathiometalates decompose to form carbon containing amorphous metal disulfides. Organic ammonium tetrathiotungstates are thermally more stable than the corresponding tetrathiomolybdates as evidenced from the thermal investigation of these complexes.

Several salts of organic ammonium tetrathiomolybdates, tetrathiotungstates and oxochromates have been structurally characterized. The salient structural features of a few structurally characterized tetrathiometalates are described below.

The crystal structures of organic ammonium tetrathiometalate consists of organic ammonium cations which are connected to tetrahedral \([\text{MS}_4]^2-\) dianions via weak H-bonding interactions (N-H-...S). In ethylenediammonium tetrathiotungstate (enH2)[WS4] [42], the W-S bond distances vary from 2.1851(14) to 2.1943(13) Å with S-W-S angles ranging from 108.66(7) to 110.08(6)° indicating small distortion of \([\text{WS}_4]^2-\) anion (Fig 1). The (enH2)[WS4] is isostructural with the corresponding ethylenediammonium tetrathiomolybdate (enH2)[MoS4] [43]. In 1,3-propanediammonium tetrathiomolybdate (1,3-pnH2)[MoS4] [44], the S-Mo-S angles vary from 108.16(3) and 110.43(3)° with Mo-S bond lengths ranging from 2.1699(8) to 2.1882(7) Å with an average of 2.1815 Å (Fig 2). The N-H-...S angles ranging from 128.74 to 162.97° indicate different degree of S...14 bond strengths (Fig 3). The W analogue [45] of (1,3-pnH2)[MoS4] shows similar type of structural features (Fig. 4). The crystal structure of N,N,N’,N’-tetramethylethylenediammonium tetrathiomolybdate (tmeh2)[MoS4] [44] (Fig. 5 and Fig. 6) and the corresponding W analogue (tmeh2)[WS4] [45] (Fig. 7) consist of (tmeh2)2+ dication and [MS4]2- dianion linked to each other via weak H-bonding interactions (N-H-...S) leading to a slight distortion of [MS4] tetrahedron. The elongation of W-S lengths due to H-bonding interactions (N-H-...S) has been also observed in crystal structure of 1,4-dimethylpiperazinium tetrathiotungstate (1,4-dmpH2)[WS4] (Fig. 8) [46].

Piperazinium tetrathiomolybdate (pipH2)[MoS4] [47] exhibits interesting structural features as S-Mo-S angles vary from 108.66(3) to 110.04(3)° and Mo-S bond distances ranges from 2.1683(8) to 2.2114(8) Å (Fig. 9). The difference between the longest and the shortest Mo-S bond distances of 0.0431 Å in (pipH2)[MoS4] is very large compared to those observed in known tetrathiometalates. The elongation of Mo-S bond distances in (pipH2)[MoS4] can be attributed to the observed short H-
bonding contacts (2.379-2.884 Å) between cation and anion, which result in an extended three-dimensional network as shown in (Fig. 9). Similar structural trends are observed in the corresponding W analogue (pipH2)[WS4] [48] (Fig. 10). The crystal structures of hydrated (trenH2)[MoS4] H2O (tren is tris (2-aminoethyl)amine) [47] and (trenH2)[WS4] H2O [48] show two types of H-bonding interactions as shown in (Fig. 11) and (Fig. 12). The two Cr complexes namely (enH2)[CrO4] and (enH2)[Cr2O7] has been structurally characterized and shown to exhibit N-H...O interactions [49].

The final chapter summarizes the results of the present work. A few of the important results are as follows:

1. A simple base promoted cation exchange method has been developed for the convenient synthesis of crystalline organic ammonium tetrathiometalates and oxochromates.
2. [MX4]2- (M= Mo, W, Cr; X= O, S) core is stable in alkaline medium.
3. Acidification of [MS4]2- core results in the formation of highly insoluble amorphous MS3 as the ultimate product.
4. The splitting of M-S bands in the IR region of tetrathiometalates has been attributed to different degree of tetrahedral MS4 distortion.
5. The shift in N-H vibrations to lower frequency in the IR spectra of organic ammonium tetrathiometalates can be attributed to H-bonding interactions.
6. The two complexes viz (trenH2)[MoS4] H2O and (trenH2)[WS4]·H2O are the first examples of structurally reported hydrated organic ammonium tetrathiometalates
8. Tetrathiotungstate complexes are thermally more stable than corresponding tetrathiomolybdates complexes.
9. Elemental analysis of thermolysis products shows considerable amount of carbon content.
10. X-ray powder pattern of thermal product indicates the formation of amorphous metal sulfides.
11. The structure of organic ammonium tetrathiometalates complexes consists of tetrahedral [MS4]2- (M= Mo or W) dianions which are connected to organic ammonium cations via weak H-bond interactions (N-H---S).
characterization of several $[\text{MS}_4]^{2-}$ complexes with different cations indicates the structural flexibility of the tetrahedral $[\text{MS}_4]^{2-}$ core.

12. The strength and number of H-bonds affect the M-S bond lengths in $[\text{MS}_4]^{2-}$ complexes while Cr-O bond lengths in oxochromates.

13. Piperazinium tetrathiomolybdate and tetrathiotungstate show maximum splitting of M-S band in IR and Raman spectra compared to other complexes indicating the maximum distortion of $[\text{MS}_4]$ tetrahedron.

14. The longest Mo-S bond length (2.2114 Å) is observed in $(\text{pipH}_2)[\text{MoS}_4]$ and longest W-S bond length (2.2147 Å) is observed in $(\text{pipH}_2)[\text{WS}_4]$ indicating maximum distortion of $[\text{MS}_4]$ tetrahedron.

15. $(\text{dbtmen})[\text{MS}_4]$ (M=Mo,W) complexes are the first examples of highly insoluble organic ammonium $[\text{MS}_4]$ compounds.

16. A convenient method has been developed for the quantitative estimation of $[\text{MS}_4]^{2-}$ core in the tetrathiometalates by using $[\text{Ni(en)}_3]\text{Cl}_2\cdot 2\text{H}_2\text{O}$.

The thesis ends with some recommendations for future work.
Selected References


XVII
Fig. 1 Crystal structure of (enH₂)[WS₄] with labeling and displacement ellipsoids drawn at the 50% probability level.

Fig. 2. Crystal structure of (13-pnH₂)[MoS₄] with labeling and displacement ellipsoids drawn at the 50% probability level.

Fig. 3. Crystal structure of (1,3-pnH₂)[MoS₄], with view along the a-axis (hydrogen bonding is shown as dashed lines).
Fig 4. Crystal structure of the anion and cation in (1,3-pnH₂)[WS₄] with labeling and displacement ellipsoids drawn at the 50% probability level.

Fig 5. Crystal structure of the anion and cation in (tmenH₂)[MoS₄], with labeling and displacement ellipsoids drawn at the 50% probability level.
Fig. 6 Crystal structure of the anion and cation in (tmenH₂)[MoS₄], with view along the a-axis (hydrogen bonding is shown as dashed lines).

Fig. 7. Crystal structure of the anion and cation in (tmenH₂)[WS₄], with labeling and displacement ellipsoids drawn at the 50% probability level.

Fig. 8 Crystal structure of the anion and cation in (1,4-dmpH₂)[WS₄], with labeling and displacement ellipsoids drawn at the 50% probability level.
Fig. 9 Crystal structure of (pipH₂)[MoS₄] with labeling and displacement ellipsoids drawn at the 50% probability level (top), with view in the direction of the crystallographic a-axis (middle) and c-axis (bottom) (hydrogen bonding is shown as dashed lines).
Fig. 10 Crystal structure of (pipH₂)[WS₄] with view of the [WS₄]²⁻ anion (top: left) and the (pipH₂)³⁺ cation (top: right) with labeling and displacement ellipsoids drawn at the 50% probability level and of the packing in the direction of the c-axis (bottom) (hydrogen bonding is shown as dashed lines).
Fig. 11 Crystal structure of (trenH₂)[MoS₄]·H₂O with labeling and displacement ellipsoids drawn at the 50% probability level (top), with view in the direction of the crystallographic a-axis (middle) and c-axis (bottom) (hydrogen bonding is shown as dashed lines).
Fig. 12. Crystal structure of (trenH₂)[WS₄]²⁻·H₂O with view of the [WS₄]²⁻ anion (top: left) and the (trenH₂)²⁺ cation (top: right) with labeling and displacement ellipsoids drawn at the 50% probability level and of the packing in the direction of the c-axis (bottom) (hydrogen bonding is shown as dashed lines).