In recent years, the chemistry of Mo/W-S complexes is an area of intense research investigations owing to the use of the group VI metal sulfides in hydrodesulfurization catalysis (HDS) [202] and the emerging importance of the layered metal disulfides in nanomaterials [203]. The soluble sulfides of the group VI metals Mo and W [98, 99] are a unique class of compounds with a wide range of metal to sulfur stoichiometries, metal oxidation states, coordination geometries and bonding modes of the sulfido ligands. The use of (NH₄)₂[MS₄] (M=Mo, W) as precursors for the soft synthesis of MS₂ nanotubes [28,29], is an important reason for the current interest in the chemistry of tetrathiometalate. Recently it has been reported that the direct pyrolysis of bis(cetyltrimethylammonium) tetrathiotungstate leads to the formation of bulk quantities of uniform WS₂ nanotubes [71]. The use of the corresponding Mo analogue has been reported to yield MoS₂. These reports indicate the emerging importance of organic ammonium salts of [MS₄]²⁻ (M = Mo,W) in material applications.

In the present work the synthesis, spectroscopy, reactivity characteristics, thermal decomposition aspects, as well as structural characterization of several new organic ammonium tetrathiometalates has been achieved. A convenient method has been developed for the high yield synthesis of crystalline tetrathiometalates. The formulation of the synthesized complexes has been arrived at based on elemental analysis, further supported by spectroscopic and X-ray structure determination. In a few cases where X-ray quality crystals could not be prepared, the formulation of the complexes is based on analytical and spectroscopic data. In this context it should be noted that a rapid method for the convenient estimation of [MS₄]²⁻ content of the new tetrathiometalates has been developed based on the high insoluble nature of [Ni(en)₂][MS₄]. The synthetic protocol used for the preparation of thiometalates has also been extended to oxochromates and two oxochromates have been characterized. A few of the important conclusions of the present work are given below:
1. A simple base promoted cation exchange method has been developed for the convenient synthesis of crystalline organic ammonium tetrathiometalates.

2. All the complexes exhibit characteristic IR spectra. The IR spectrum of an organic ammonium tetrathiomolybdate is identical to that of the corresponding W analogue excepting that the signals below 500 cm\(^{-1}\) are shifted to lower energies in the W compound. The usefulness of IR spectra for the characterization of the tetrathiometalate as well as the organic cation has been discussed in the previous chapter.

3. The structural characterization of the complexes shows that an organic ammonium tetrathiomolybdate is isostructural with its corresponding W analogue.

4. The structures of the synthesized tetrathiometalates can be described as consisting of tetrahedral \([MS_4]^2-\) (M = Mo, W) ions which are linked to the organic ammonium cations via weak H-bonding interactions in the form of S...H-N bonds.

5. The strength and number of H-bonding interactions affect the M-S bond lengths as evidenced by the observation of long and short M-S bond distances for every complex.

6. With a view to understand the importance of the H-bonding interactions several organic ammonium tetrathiometalates have been characterized. For this purpose a variety of organic amines which differ in terms of this potential H-bonding donors and steric bulk have been employed in this study.

7. The two tetrathiometalates viz \((\text{trenH}_2)[\text{MoS}_4]\cdot\text{H}_2\text{O}\) and \((\text{trenH}_2)[\text{WS}_4]\cdot\text{H}_2\text{O}\) are the first examples of structurally characterized hydrated organic ammonium tetrathiometalates [83,87]. Both exhibit two types of interactions namely S...H-N and S...H-O. The S...H-O interactions in these complexes appears to be weaker compared to the S...H-N interactions in terms of their ability to elongate M-S bonds.

8. A comparative study of the structural features of several tetrathiometalates which includes known tetrathiometalates, in addition to the new ones described herein has been made to provide a possible explanation for the observed distinct M-S bond distances.
9. Based on the comparative study, it can be inferred that the difference between the longest and the shortest M-S bond can be considered as an important factor to describe the observed distortion.

10. The compounds (pipH2)[MS4] exhibit the maximum Δ value for the tetrathiomolybdate series while the corresponding W analogue exhibits the maximum Δ value for [WS4]2- complexes.

11. When the Δ value is more than 0.030 Å this can be considered as a pronounced distortion of the MS4 tetrahedron as evidenced by the splitting of the asymmetric stretching vibration in the IR spectra.

12. All the tetrathiometalates can be thermally decomposed to the corresponding amorphous sulfides. Tetrathiotungstates are thermally more stable than the corresponding tetrathiomolybdates.

13. Many of the organic ammonium salts of tetrathiometalates can be decomposed in a single endothermic event resulting in the formation of carbon contaminated MS2 unlike the ammonium salts which exhibit an endothermic event followed by an exothermic process to form MS2. The X-ray powder pattern revealed the amorphous nature of the residues.

14. The isostructural complexes viz (dbtmen)[MS4] (M=Mo,W) are the first examples of highly insoluble organic ammonium tetrathiometalates.

15. The reaction of soluble tetrathiometalate with [Ni(en)3]Cl2.2H2O results in the formation of the highly insoluble [Ni(en)3][MS4] (M = Mo, W) complexes in quantitative yield. The formation of the insoluble [Ni(en)3][MS4] has been used as a convenient method for the quantitative estimation of [MS4]2- content.

16. The structurally characterized oxochromates exhibit N-H...O interactions that stabilize the overall structure.