CHAPTER 4

SUMMARY AND CONCLUSIONS

The study 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) and the emerging importance of the layered metal disulfides in nanomaterials. The use of \((\text{NH}_4)_2[\text{MS}_4]\) (M=Mo, W) as precursors for the soft synthesis of \(\text{MS}_2\) nanotubes, is an important reason for the current interest in the chemistry of tetrasulfidometalate. Recently it has been reported that the direct pyrolysis of bis(cetyltrimethylammonium) tetrasulfidotungstate leads to the isolation of bulk quantities of uniform \(\text{WS}_2\) nanotubules [30]. The use of the corresponding Mo analogue has been reported to yield \(\text{MoS}_2\). The reactivities of the sulfidometalates and their application in complex chemistry are important since they display unique ligand properties. Tetrasulfidometalates stabilized by organic ammonium cations are employed as precursor for the synthesis of catalytically relevant \(\text{MoS}_2\) and \(\text{WS}_2\) materials. Mo-S compounds like \([\text{((PhCH}_2)\text{N(C}_2\text{H}_5)_3]_2[\text{MoS}_4]\), \((\text{NH}_4)_2[\text{MoS}_4]\) are used as sulfur transfer reagents, while oxidochromates are used as oxidizing agents in synthetic organic chemistry. Recent work by the Jakobsen group on the use of \((\text{X})_2[\text{MS}_4]\) (\(\text{X} = \text{NH}_4, \text{Rb}, \text{Cs}, -\text{CH}_3\text{NH}_3; \text{M} = \text{Mo}, \text{W}\)) for advancement in natural abundance solid state \(^{33}\text{S}\) MAS NMR spectroscopy has added a new dimension to the chemistry of the group VI sulfide compounds [177,178]. The sulfur compounds of Mo and W charge balanced by organic ammonium cations exhibit a rich structural chemistry in terms of the several weak H-bonding interaction between the sulfidometalate anion and the organic ammonium cation [94-123] These reports indicate the emerging importance of organic ammonium salts of \([\text{MS}_4]^{2-}\) (M = Mo, W) in material applications.

The synthesis, spectroscopy, reactivity characteristics, thermal decomposition aspects, as well as structural characterization of several new organic ammonium tetrasulfidometalates, a few oxidometalate and two organic thiosulfates have been achieved in the present investigation. A simple and convenient method has been developed for the high yield synthesis of crystalline tetrasulfidometalates. The formulation of the synthesized compounds has been arrived on the basis of elemental
analysis, further supported by spectroscopic studies. Most of the compounds were investigated by single crystal X-ray structure determination. For compounds where the crystals obtained were not suitable for single crystal X-ray determination studies were limited to X-ray powder pattern. The synthetic protocol used for the preparation of thiometalates has also been extended to oxidometalates and thiosulfates, and are well characterized. A few of the important conclusions of the present work are listed below:

1. All the characterized compounds of organic ammonium tetrasulfidomolybdate are isostructural with its corresponding W analogue as evidenced by the XRD powder pattern.

2. A simple base promoted cation exchange method has been developed for the convenient synthesis of crystalline organic ammonium tetrasulfidometalates.

3. All the compounds exhibit characteristic IR spectra. The IR spectrum of an organic ammonium tetrasulfidomolybdate 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.

4. The crystal structure of the synthesized tetrasulfidometalates can be described as consisting of tetrahedral [MS$_4$]$^{2-}$ (M = Mo, W) anions which are linked to the organic ammonium cations with the aid of weak N-H$\cdots$S and C-H$\cdots$S interactions.

5. A variety of organic amines which differ in terms of their potential H-bonding donors have been utilized with a view to understand the importance of the H-bonding interactions in several organic ammonium tetrasulfidometalates.

6. The strength and number of H-bonding interactions affect the M-S bond lengths as evidenced by the observation of lengthening of M-S bond distances. $\Delta$, the difference between the longest and the shortest M-S bond can be considered as an important factor to describe the observed distortion. Further, if the $\Delta$ value is greater than 0.033 Å then this can be considered as a threshold value for the distortion of the MS$_4$ tetrahedron which can be observed as splitting of the M-S vibration in the IR spectra.

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7. For the compound (dienH$_2$)[MoS$_4$], it exhibits the maximum $\Delta$ value for the corresponding tetrasulfidomolybdates series while the corresponding W analogue exhibits the maximum $\Delta$ value for [WS$_4$]$^{2-}$ compounds.

8. The present work reports synthesis, structural aspects and H-bonding characteristics of the first examples of tetrasulfidometalates charge balanced by chiral organic ammonium cations.

9. The series of (dienH$_2$)[MS$_4$] compounds serve as an example of polymorphism to be observed in tetrasulfidometalate complexes.

10. The reaction of N-methylpiperazine with [MS$_4$]$^{2-}$ results in the formation of hydrate-polymorphism to be observed in such tetrasulfidometalate complexes.

11. The thermal decomposition of most of the tetrasulfidometalates results in carbon contaminated metal sulfide residues which are amorphous in nature. Tetrasulfidotungstates are thermally more stable compared to the corresponding organic ammonium salts of tetrasulfidomolybdates.

12. Thermal decomposition of tetrasulfidometalates salts of cations such as benzyltriethylammonium and benzyltrimethylammonium cation results in the formation of amorphous porous-carbon contaminated metal sulfide residues.