TETRASULFIDO METALLATES

A project report submitted to

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MASTER OF SCIENCE IN CHEMISTRY

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CERTIFICATE

This is to certify that the dissertation entitled “**Tetrasulfido Metallates”** is bonafied work carried out by Mr. Sainand Sadanand Amonkar under my supervision in partial fulfilment of the requirement for the award of the degree of Master of Science at School of Chemical Sciences, Goa University.

Dr. Sunder N. Dhuri

Project Guide

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DECLARATION

I hereby declare that embodied in this report entitled “**Tetrasulfido Metallates**” was carried out by me during the year 2021-2022 under the guidance of Dr. Sunder N. Dhuri. In keeping with the general practices of reporting scientific observations, due to acknowledgements have been made whatever the work described is based on the findings of other invesgators.

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ACKNOWLEGEMENT

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I wish to thank Prof. Dr. Vidhyadatta Verenkar, Dean of School of Chemical sciences, Goa University.

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Mr. SAINAND SADANAND AMONKAR

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1.1. INTRODUCTION

Tetrasulfido Metallates

General Formula: $[MS_4]^{2-}$

M = Mo(IV) or W(IV) i.e., Tetrasulfido Molybdate & Tetrasulfido Tungstate: $(MoS4)^{2-}$ & $(WS4)^{2-}$

$$(MoS4)^{2-} + NH_3 \xrightarrow{} (NH4)_2(MoO_4) \xrightarrow{H_2S} (NH_4)_2(MoS_4)$$

Ammonium tetrathiomolybdate[1] is the chemical compound with the formula $(NH_4)_2MoS_4$. This bright red ammonium salt is an important reagent in the chemistry of molybdenum and has been used as a building block in bioinorganic chemistry. The thiometallate anion has the distinctive property of undergoing oxidation at the sulfur centers concomitant with reduction of the metal from Mo(VI) to Mo(IV). Its main hazard is it's toxicity. Its Molar Mass is 260.28 g/mol and Melting Point is ~ 155 °C.

Another name for Ammonium tetramolybdate is *'Ammonium thiomolybdate'*.

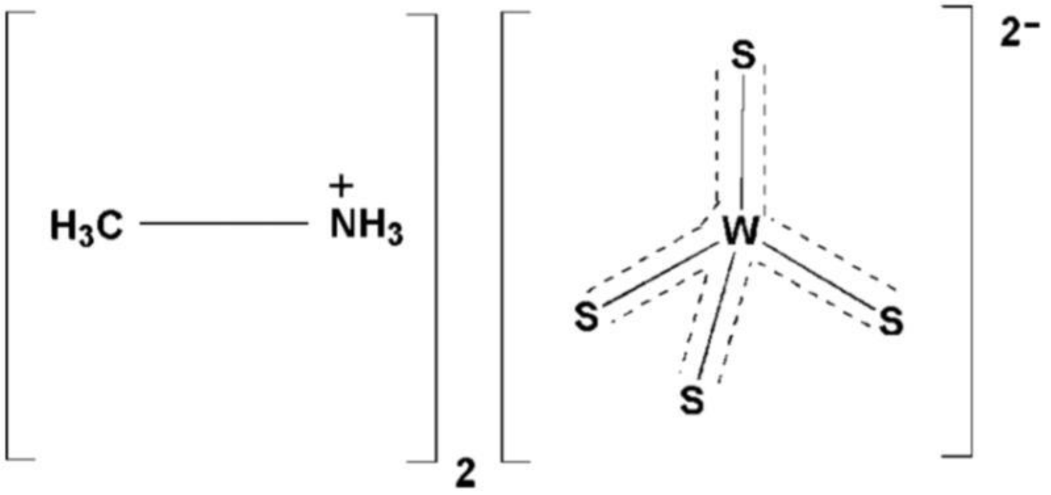
The entitled compound, $(C_3H_{10}N)_2[MoS_4]$, was synthesized by passing a rapid stream of H(2)S into an aqueous isopropyl-amine solution of molybdic acid. The entitled compound is isotypic with the corresponding W-analogue $(C_3H_{10}N)_2[WS_4]$; its structure consists of a slightly distorted tetra-hedral $[MoS(_4)]^{2-}$ dianion and two crystallographically independent isopropyl-ammonium cations, with all atoms located in general positions. The cations and anion are linked by weak N-H – S and C-H – S inter-actions, the strength and number of which can explain the observed Mo-S bond distances.

1.2. Tetrasulfido Tungstate

Example:

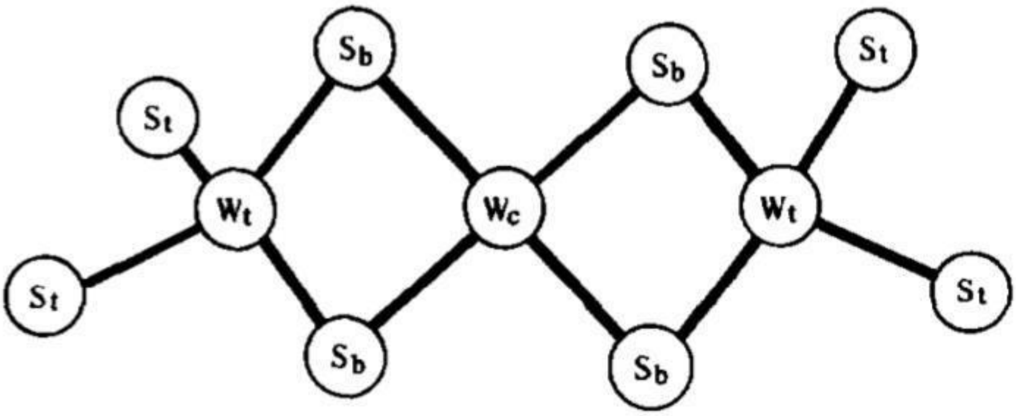
$$WO_3 + NH_3 \xrightarrow{H_2S} (NH_4)^{2-}(WS_4)$$

Compound, $(CH_6N)_2[WS_4]$, was synthesized by the reaction of ammonium tetrasulfidotungstate(VI) with aqueous methylamine. The title compound is isotypic with the corresponding Mo analogue $(CH_6N)_2[MoS_4]$, and its structure consists of a slightly distorted tetrahedral $[WS_4]^{2-}$ dianion and two crystallographically independent methylammonium ($MeNH_3$) cations, all of which are located on crystallographic mirror planes. The tetrasulfidotungstate anions are linked to the organic cations via hydrogen-bonding interactions.



$(MoSi_4)^2$ and $(WS_4)^2$ these two Thioanions[2] have been often Used as bidentate ligands to obtain a variety of Metal complexes. Many complexes Of the type $[M(XS)_4]^{2-}$ (M = Fe, Co, Ni and Zn) (X = MO or W) has been isolated and characterized.

The structure of this type of metal complex consists of two (XS4)2- anions coordinating as Bidentate ligands with the metal (M). A square-Planar or tetrahedral arrangement is possible Around the central metal. This class of compounds Is of interest from the theoretical point of View and also has possible catalytic significance.



A square planar geometry of Tungsten is obtained by Bhaduri and Ibers for the first time, they were successful in isolating a diamagmetic complex anion $[W(WS_4)_2]^{2-}$ X-ray determination has indicated that the complex ion has a symmetry approximating D2h with a Tetrahedral coordination around the terminal W. The central tungsten (W,) has a square planar coordination of sulphur with a very slight tetrahedral distortion.

1.3. The Chemical behavior of free and CTA interlayered $(MoS_4)^{2-}$ anions

It was found that a homogenous reaction[2] between ATTM and hydrazine In aqueous medium leads to the molybdenum reduction with formation of Molybdenum disulfide the data obtained in present studies shows that in the similar reaction conditions (temperature, pH, hydrazine, concentration) transformation of $[MoS_4]^{2-}$ situated in between the CTA layers also proceeds but in the different way. Difference between two processes can be illustrated by the following redox reactions:

$$[Mo^{(iv)}S_4]^{2-} + 2e- \longrightarrow Mo^{(iv)} S_2 + 2S^{2-}$$

$$2[Mo^{(vi)} S_4]^{2-} + 2H_2O - 2e- \longrightarrow [Mo^{(v)}O_2S_2(S_2)_2]^{2-} + 2H_2S$$

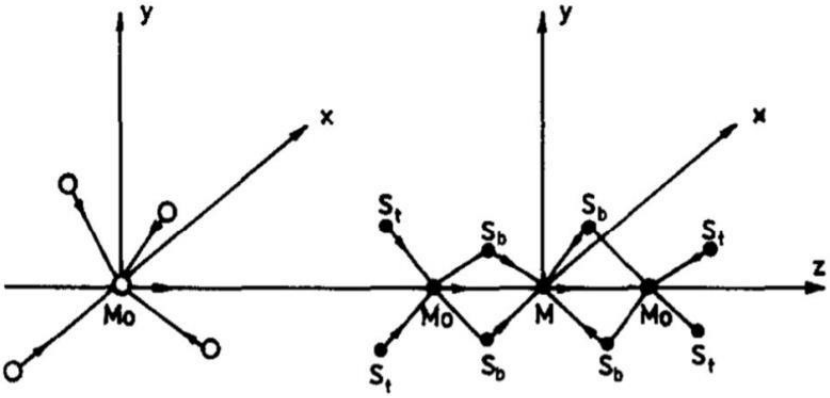
Intensive studies in transition metal complexes with $[MoS_4]^{2-}$and $[WS_4]^{2-}$ thioanions[3] acting as bidentate chelating ligands in the trimetallic $[M(MoS_4]^{2-}$-n type complexes were initiated by Miller et al. One can observe an increasing interest in these compounds.

Their investigation has been stimulated by two factors:

i) the discovery that some redox-proteins contain transition metal ions and the ‘labile’ sulfur in their active sites, and

ii) the conformation that there exist multimetal complexes of this type with a variety of electron populations. They reported the results of our theoretical invetigations of Fe and Co complexes with tetrathiomolybdate ions for various formal oxidation states of a central atom in this.

Following is the geometry and the coordinate system of IMoS41 -’ ion, Td symmetry, and $[M(MoS_4)^{2-}$ complexes, D_{td} symmetry.



The designing of selective and efficient adsorbent for removal of heavy metals from wastewater of diverse chemistry is a challenging task for researchers[4]. Herein[5], FeMgAl derived from layered double hydroxides (LDH) with different intercalated anions $(CO_3)^{2-}$, $(NO)^{3-}$, $(S_5)^{2-}$ and $(MoS_4)^{2-}$ as selective adsorbents were evaluated by considering capturing heavy metals from a complex aqueous environment such as: i) adsorption of single metals ions from a mixture of Ag^+, Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and adsorption of heavy metals in the presence of huge amount of Ca^{2+}, Mg^+, Na^+, Cl^-, NO^{3-} and $(SO_4)^{2-}$ ions, ii) adsorption under different solution pH. iii) solutions with high salinity etc.

1.4. $(MoS_4)^{2-}$

It have been introduced moiety into the lamellar layers of Ca^4 0.66 Al $0.34(OH)_2(NO_3)$ 0.34·yH2O to fabricate Ca 0.66 Al $0.34(OH)_2(MoS_4)0.17·yH_2O$ ($CA-MoS_4·LDH$), a stable and efficient adsorbent for removal of two envoy Fluoroquinolones (FQs), Ciprofloxacin (CIP) and Ofloxacin (OFL), from contaminated aquatic sources. Various characterization tools, such as X-ray diffraction (XRD), Scanning electron microscopy, Energy dispersive X-ray spectrometer, transmission electron microscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy and Thermogravimetric analyses etc. Were applied to confirm structural and compositional changes during the synthesis and adsorption properties of CA-MoS4·LDH. The efficiency of adsorbent was investigated by evaluating different parameters including contact time, pH of solution, initial concentration of pollutant, and effect of temperature. By using $CA-MoS_4·LDH$ as adsorbent, we found more efficient removal of CIP than that of OFL due to the steric hindrance. The highest uptake of 707.20 mg/g and 476.74 mg/g of CIP and OFL, respectively, was found at pH of 6 with improved kinetics and easily reusability for these representative antibiotics models so far. Removal kinetics of both FQs were found to better follow the pseudo-second-order kinetic model than the pseudo-first-order. The Langmuir adsorption isotherm was employed to understand the removal process, suggesting monolayer chemisorption mechanism. The adsorbate-adsorbent interaction revealed remarkable features originate from the combination of weak hydrogen bond interaction between thio group and NH^{2+}

group of antibiotic and electrostatic interaction between positive LDH layer and COO^{-} group of antibiotic as well, and anion exchange mechanisms, which were also confirmed by XRD, FTIR, XPS and Raman spectrum etc. Obtained after adsorption. It is proposed that all $(MoS_4)^{2-}$ moiety offers stability to the CA-MoS_4·LDH structure to avoid its solubility under ambient environments.

For the synthesis of $(NH_4)_2MoS_4$, it was synthesized by slowly dissolving $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.024 mol) in 200 mL Ammonia solution (25 % wt)[6]. A freshly prepared H2S was introduced to this solution for 1h. giving red-green shimmery crystals product. Crystals are washed with cold distilled water, ethanol, and diethyl ether. The yield was 62 %. The $(MoS_4)^{2-}$ anion of the $(NH_4)_2MoS_4$ precursor was exchanged with NO_3 anion of the white CaAl-LDH to obtain the CA-MoS_4•LDH (red brown). Typically, 0.3 g of CaAl-LDH and 0.3g of $(NH_4)_2MoS_4$ were dispersed in 10 mL of degassed deionized water, and the obtained suspension was allowed to sonicate for 5 hours. The resulting orange colored solid was filtered and washed with deionized water and then acetone, and finally air-dried, to get the red brown product LDH (red brown). Typically, 0.3 g of CaAlLDH and 0.3G of (NH4)2MoS4 were dispersed in the 10 mL degassed deionized water, and the obtained Suspension was allowed to sonicate for 5 hours. Filtering the resulting orange colored solid, Washed with deionized water and then acetone, and finally air-dried, to get the red brown product All adsorption experiments were carried out in 150 mL of conical flask by mixing 100 mg/L of CA-MoS_4•LDH with 100 mL CIP and OFL solution in a thermostatic shaker at different temperature. The initial pH of respective solutions was adjusted to a certain value by using HCl and NaOH solution by pH meter. After adsorption, the mixture was filtered and analyzed for the final concentration of antibiotics by a high-performance liquid chromatography. Paper 3 The designing of selective and efficient adsorbent for removal of heavy metals from wastewater of diverse chemistry is a challenging task for researchers. Herein, FeMgAl derived from layered double hydroxides (LDH) with different intercalated anions ($(CO_3)^{2-}$,$(NO_3)^{-}$, $(S_5)^{2-}$ and $(MoS_4)^{2-}$) as selective adsorbents were evaluated by considering capturing heavy metals from a complex aqueous environment such as: 1) adsorption of single metals ions from a mixture of

Ag^+, Hg^{2+}, Pb^{2+},Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} [7]) adsorption of heavy metals in the presence of huge amount of Ca2+,Mg+,Na+, Cl−, NO^{3-} and $SO4^{2-}$ ions, 3) adsorption under different solution pHs, 4) solutions with high salinity etc. Out of the studied materials, fast kinetics, record capacities (582 for Hg^{2+} and 565 mg/g for Ag^+) with enormous Kd values (1.0×10^8 – 2.5×10^7 placed FeMgAl-MoS4 (Fe-MoS4 LDH) as the most selective and promising material. FeMgAl-S_5 (Fe-S5 LDH) was also impressive due to its good capacities (279 mg/g for Hg^{2+} and 341 mg/g for Ag^+ ions) with Kd values (8.3×10^5– 1.0×10^3 In contrast, FeMgAl-CO_3 and FeMgAl-NO_3 (Fe-CO_3 LDH and Fe-NO_3 LDH) showed very poor selectivity, lower capacities and very small Kd values. Furthermore, Fe-MoS_4 LDH and FeS_5 demonstrated negligible efficiency loss in the presence of competitive cations/anions or with change in solution pH. As confirmed by X-ray Diffraction (XRD) and Fourier transformed Infrared (FTIR) analysis, a mechanism for adsorbed metals in the form of various coordinated complexes inside LDH layers was proposed for Fe-MoS4 or Fe-S_5 LDHs. In contrast, a dominant precipitation mechanism as metal-hydroxide or metal-carbonate was suggested for $FeCO_3$ and Fe-NO_3 LDHs.

Jia-Cheng E, Kiran Gupta et al.[4] in this paper the chemist introduced $(MoS_4)^{2-}$ moiety Into Lamellar Layers , For removal of two anvoy fluoroquinolones (FQs)
To confirm structural and the compositional changes during synthesis they use X ray diffraction techniques, scanning electron microscopy, transmission electron microscopy, Xray photo electric microscopy, Raman spectroscopy, Thermogravimetric analysis etc. The Langmuir adsorption isotherm was employed to understand the removal process. It is Proposed that all (MoS4) 2- moiety offers stability to the "CA-MOS_4-LDH structure to avoid its solubility under ambient environments.

The synthesis of the new dithiolene complexes[5], $[\{(MeOOC)_2C_2S_2\}_2Mo(\mu^2\text{-}S)]^{2-}$ and $[OMo(S_2C_2(COOMe)_2)_2]^-$, is reported. These complexes are obtained by the reaction of dicarbomethoxyacetylene (DMA) with either $[(S_4)Mo(S)(\mu^{2-}S)_2Mo(S)(S_4)]^{2-}$ or $[(CS_4)Mo(S)(\mu^{2-}S)_2Mo(S)(CS_4)]^{2-}$ and $[OMo(S_4)_2]^{2-}$, respectively. The reaction of $[(S_4)Mo(O)(\mu2\text{-}S)2Mo(O)(S_2)]2-$ with DMA results in the new dithiolene complex

$[\{(MeOOC)_2C_2S_2\}Mo(O)(\mu^{2\text{-}}S)]^{-2}$, which is the isomeric form of the vinyl disulfide complex obtained in the reaction of the $[(S2)Mo(O)(\mu_2\text{-}S)2Mo(O)(S_2)]^{2-}$ complex with DMA. The difference in reactivity between the two complexes that contain the same $[Mo_2O_2S_2]^{2+}$ core is attributed to the intrinsically different reactivity characteristics of the S_{2-4} and S_{2-2} ligands. As a result of Mo-S dπ-pπ bonding an alternation in the S-S bond lengths is observed in virtually all of the structurally characterized Mo-S_4 units. The consequent weakening of the S-S bonds adjacent to the MoS bonds allows for the ready dissociation of S02 from the Mo-coordinated S_{2-4} ligands[8]. This weakening also accounts for the facile formation of dithiolenes in cycloaddition reactions of alkynes with the Mo-S_4 units. By comparison[9], the SS bond in side-on Mo-coordinated S_{2-2} ligands is strengthened as a result of depopulation of the ligand π*-orbitals. Reactions of the latter with alkynes do not proceed by cycloaddition. Instead, insertion into the MoO bond has been reported for at least one such reaction[10].

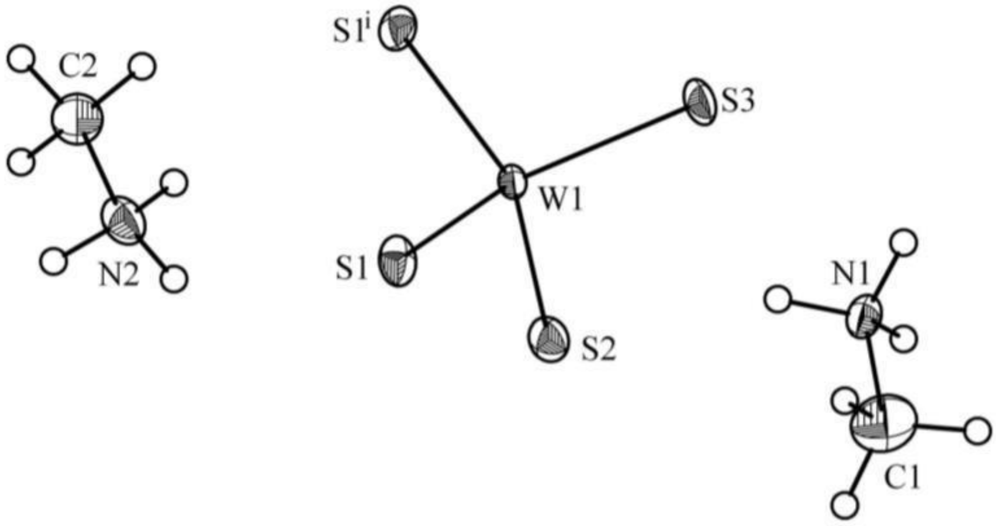
Series of FeMgAl-LDHs (Fe-LDHs) with different intercalated anions (CO3)2− ,NO3−, S52− and MoS42− were first synthesized. Different characterization techniques such as XRD, FTIR, Scanning Electron Microscopy (SEM), Carbon Hydrogen Analyser (CHN), Thermal Gravimetric Analysis (TGA) and X-ray Photoelectron Spectroscopy (XPS) were applied to confirm the synthesis of these materials. These materials were evaluated as potential adsorbent by capturing individual heavy metal ions from mixture of eight heavy metals solution containing huge amount of background electrolytes (i.e. Ca2+, Mg2+, Na+, Cl−, NO3− and SO42− and real wastewater collected from different industries. Furthermore, detail kinetic and isothermal study were also considered for evaluation of these materials.

Based on the wide effective pH, record high capacity and high Kd values, Fe-MoS4 was placed as best material for heavy metals capturing. Additionally, a distinct heavy metals adsorption mechanism for Fe-MoS4 and Fe-CO3 LDH taken as bench materials was also proposed.

Bis(methylammonium) tetrasulfidotungstate(VI)

Structure of a new organic $[WS_4]^{2-}$ compound containing methylammonium as counter cation

The title compound is isostructural with $(NH_4)_2[WS_4]$, $Cs_2[WS_4]$, $Rb_2[WS_4]$, and $(CH_6N)_2[MoS_4]$. The structure consists of a Discrete tetrahedral $[WS_4]^{2-}$ ion and two crystallographically independent methylammonium cations, all of which are located on crystallographic mirror planes so that each half of these ions make up the asymmetric unit. The bond Lengths and bond angles of the organic cations are in good agreement with the reported values for the isotypic Mo Compound. The WS_4 tetrahedron is slightly distorted with S—W—S angles between 108.46 ° and 110.45°



The W—S bond lengths range from 2.1862 to 2.2010Å

The observed difference Δ between the longest and the shortest W—S bonds of 0.0148 Å in the title compound is slightly shorter than the value of 0.0199 Å in the analogous Mo compound $(CNH_6)_2[MoS_4]$.

Experimental $(NH_4)_2[WS_4]$ (1 g) was dissolved in 40% methylamine (5 ml) and water (2 ml) and filtered. The clear yellow filtrate was Left undisturbed for crystallization. After a day crystalline blocks of the title compound separated. The product was filtered, washed with ice-cold water (1 ml), followed by 2-propanol (5 ml) and diethyl ether (10 ml) and dried. Yield: 1.1

Treatment of Wilson Disease With Ammonium Tetrathiomolybdate

The initial treatment of patients with Wilson disease who present with neurologic symptoms is problematic. Among the 3 commercially available anticopper agents, penicillamine often makes about half of these patients irreversibly neurologically worse, trientinehydrochloride is untested but its actions are much like those of penicillamine, and zinc is too slow acting to counter this Ammonium tetramolbdate is used .

Tetrathiomolybdate acts differently than previous anticopper drugs. It forms a tripartite complex with copper and protein that is very stable.5-8 Given with food,tetrathiomolybdate complexes food copper with food protein, rendering that copper, along with endogenously secreted copper in saliva, gastric juice, and intestinal secretions, unabsorbable. This puts the patient in an immediate negative copper balance. Given away from food, tetrathiomolybdate is absorbed into the blood and there complexes freely available and potentially toxic copper with blood albumin. This complexed copper cannot be taken up by cells and is therefore nontoxic. The lightly bound and potentially toxic copper of organs is in equilibrium with that in the blood, and further copper toxicity in various organs in Wilson disease is quickly stopped, generally in 1 to 2 weeks, with tetrathiomolybdate therapy.

1.7. Conclusion

Tetrasulfido Molybdate Chemical properties of [MoS4]2- anions are substantially changed in surrounding them by CTA+ Cations. Thiomolybdate anions can be easily reduced by aqueous hydrazine to MoS2, wherein in similar conditions, being bound with an organic CTA+ Cations, they are shown to become [Mo2O2S2Mo2O2S2(S2)2]2- Ammonium tetramolbdate is used for the treatment of Wilson disease. Ammonium Tetrathiomolybdate as available in most volumes. High purity, and a nanopowder forms may be considered to produces to many standard grades when applicable, including Mil Spec (military grade); ACS, Reagent and Technical Grade; Food, Agricultural and Pharmaceutical Grade; Optical Grades and follows applicable testing standards. Also availability of Typical and custom packaging . Ammonium molybdate is used as pigments, agricultural fertilizer, color lakes and fabric fire retardant agent. It is also used as a raw material for the production of molybdenum wire, ceramic glazes and other molybdenum compounds. it is used in photography, ceramics and paints. The CA-MoS4 LDH contemplated as novel adsorbent with its better kinetics, huge adsorption capacity, significant stability, and excellent reusability. Thio-based functional group improved . the stability of CA-MoS4 LDH for practical

1.8. REFERENCES

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