

ESR Spectral Characterisation of Mn doped Zn (II) Trisethylenediamine Sulfidometalate Complexes

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Abstract: Aqueous reaction of Zn(II) and Mn(II) salts with ammonium tetrasulfidometalate $(\text{NH}_4)_2[\text{MS}_4]$ ($M = \text{Mo}, \text{W}$) in the presence of ammonia or ethane 1,2-diamine (en) or propane 1,2-diamine (1,2-pn) results in the formation of $[\text{M}'(\text{L})_n][\text{MS}_4]$ ($M' = \text{Zn}$ or Mn ; $L = \text{NH}_3$ or en or 1,2-pn). Using this strategy, Mn doped Zn complex of formula $[\text{Zn}_{0.99}\text{Mn}_{0.01}(\text{en})_3][\text{MS}_4]$, which exhibits characteristic hyperfine ESR spectra have been synthesized. The synthetic aspects, spectral and thermal characterization are described..

Keywords : Coordination chemistry, Tetrasulfidomolybdate, Zinc, Manganese, Hyperfine Spectrum

I. INTRODUCTION

The soluble sulphides of group VI metals Mo and W are unique as they exhibit a wide range of metal to sulfur stoichiometries, metal oxidation states, coordination and binding modes of sulfido ligands. Tetrasulfidometalates find use in therapy² and are employed as sulfur transfer reagents in organic syntheses³. The use of alkali metal and organic ammonium tetrasulfidometalates as useful probes for the advancement of ³³S solid state MAS NMR technique has added an entire new dimension⁴. The ammonium salts of $[\text{MoS}_4]^{2-}$ or $[\text{WS}_4]^{2-}$ routinely used as a starting material for the syntheses of a variety

of structurally diverse Mo-S and W-S compounds, can function as pure inorganic ligands forming S-bridged heterometallic compounds⁵. The ability of $[\text{MoS}_4]^{2-}$ to coordinate transition metal centers like Cu^+ has led to its use as components in clusters and networks⁶.

Chemistry of formation of organic Tetrasulfidometalates which contain partially protonated organic amines as cations for charge balance has been exhaustively investigated by Srinivasan et al⁷. Recent addition to this structurally rich chemistry is the formation of two new hmt adducts $(\text{NH}_4)_6[\text{MS}_4]_3 \cdot (\text{hmt})_4$ [$M = \text{W}$ (1), $M = \text{Mo}$ (2)]. Ammonium tetrathiotungstate and bis(cetyltrimethylammonium) tetrathiotungstate are used as precursors for the soft synthesis of WS₂ nanotubes^{9,10}. The tetrahedral tetrasulfidometalates $[\text{MS}_4]^{2-}$ ($M = \text{Mo}, \text{W}$) are well known for their use as starting materials for the preparation of a variety of metal sulfur compounds including hydrodesulfurization (HDS) catalysts¹¹. It has been reported

that the HDS activity is enhanced when a bivalent 3d metal like Ni(II) or Co(II) is added to Mo or W based sulphide catalysts and also that the active phase contains M'-Mo-S-units ($M' = \text{Ni}, \text{Cu}$)¹². A material with the stoichiometry $[\text{Ni}(\text{en})_3]\text{MoS}_4$ has been determined using a single crystal, prepared solvothermally¹³ and is characterized as an HDS precursor¹⁴. The highlight of this work, is the isolation of Mn doped $[\text{Zn}(\text{en})_3][\text{MS}_4]$ ($M = \text{Mo}, \text{W}$) which exhibits characteristic hyperfine ESR spectrum. It has been documented that the reaction of bivalent metal ions like Zn^{2+} with $[\text{MS}_4]^{2-}$ leads to the formation of insoluble sulfides¹⁵. In this work, we have investigated the reactions of the bivalent metals Zn(II) and Mn(II) with $(\text{NH}_4)_2[\text{MS}_4]$ ($M = \text{Mo}, \text{W}$) in the presence of ammonia and two organic diamines, ethane 1,2-diamine (en) or propane 1,2-diamine (1,2-pn) which results in the formation of $[\text{M}'(\text{L})_n][\text{MS}_4]$. The complexes are characterized on the basis of elemental analysis, IR, UV-vis, ESR, and thermal studies. This report indicates the emerging importance of $[\text{M}'(\text{L})_n][\text{MS}_4]$ compounds which when decomposed at controlled temperature results into the formation of mixed metal sulphides which are potential materials and next generation catalysts.

II. EXPERIMENTAL

A. Materials and methods

The starting materials $(\text{NH}_4)_2[\text{MS}_4]$ ($M = \text{Mo}, \text{W}$) were prepared by literature method⁹. Infrared spectra of the synthesized complexes were recorded (as KBr pellet) on a Shimadzu (IR Prestige-21) FTIR spectrometer at a resolution of 4 cm^{-1} referenced to polystyrene bands. UV-visible spectra were recorded in the region 200-800 nm using SHIMADZU UV-2450 UV-VIS spectrophotometer. ESR spectra were recorded at room temperature using a Varian E-109 spectrometer operating at X-band using DPPH as frequency calibrant. X-ray powder pattern were recorded on a PHILLIPS HOLLAND, PW-3710 diffractometer using Cu-K_α radiation. TG/DTA studies were performed on a SDT-2960 Thermal Analyser. Isothermal weight loss studies were performed in a temperature controlled furnace.

B. Synthesis of Mn (II) doped $[\text{Zn}(\text{en})_3][\text{MoS}_4](1)$

The reaction of an aqueous solution containing a mixture of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (284.66 mg, 0.99 mmol) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (1.98 mg, 0.01 mmol) in water (~20 ml) with

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(NH₄)₂[MoS₄] (260 mg, 1 mmol) or (NH₃)₂(WS₄) (348 mg, 1 mmol) in water (15 ml) and ethylenediamine (~1.0 ml), resulted in the immediate precipitation of bright red orange colored [Zn_{0.99}Mn_{0.01}(en)₃][MoS₄] (1) or the yellow W compound [Zn_{0.99}Mn_{0.01}(en)₃][WS₄] (1a). These products were isolated as earlier.

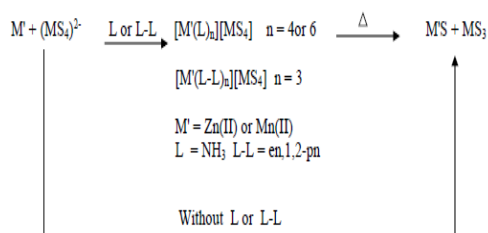
(1) IR data (νN-H)_{as} 3292, (νN-H)_s 3234, 2929, 2878, 1562, 1457, 1364, 1325, 1002, 630, 481, (νMo-S)472 cm⁻¹. UV-Vis data (water) : 259 nm, 320 nm, 474 nm. Anal. Calc. C, 15.34; H, 5.15; N, 17.89; S, 27.30; Zn, 13.92%. Found: C, 16; H, 4.78; N, 17.38; S, 28.00; Zn, 14.10%. esr: g, 2.03; A, 86. (1a) IR data (νN-H)_{as} 3295, (νN-H)_s 3238, 2928, 2879, 1564, 1457, 1368, 1325, 1002, 634, (νW-S) 459 cm⁻¹. UV-Vis data (water) : 282nm, 395 nm. Anal. Calc. C, 12.92; H, 4.34; N, 15.07; S, 23.00; Zn, 11.60%. Found: C, 13.30; H, 4.46; N, 14.78; S, 23.30; Zn, 11.55%. esr: g, 2.01; A, 82

Synthesis of [Zn(L)_n][MS₄] (L = NH₃, (en), (1,2-pn) and synthesis of [Mn(L)_n][MS₄] (L = NH₃, (en), (1,2-pn) is carried out as per the procedure given in supplementary data (S1).

III. RESULTS AND DISCUSSION

A. Synthetic aspects

It is well documented¹⁵ that the aqueous reaction of bivalent 3d metal ions (M')²⁺ with [MS₄]²⁻ results in the precipitation of a mixture of X-ray amorphous 3d metal sulfide and MS₃ (see Scheme 1). However, in the presence of a counter cation like (PPh₄)⁺, bis(tetrasulfidometalato) complexes of the type [M'(MS₄)₂]²⁻ (M' = Fe, Co, Ni, Zn) charge balanced by the bulky cation are obtained¹⁷. Unlike other 3d metal ions, reaction of aqueous solution of Mn(II) with [MS₄]²⁻ neither immediately precipitates a mixture of amorphous metal sulfides nor forms any Mn-tetrasulfidometalate complexes in the presence of organic cations¹⁸.



Scheme 1. Synthetic methodology

In view of the fact that [MS₄]²⁻ core is stable in an alkaline medium and does not retain its identity in acidic medium undergoing various reactions, the formation of insoluble sulfides can be attributed to the acidic nature of the aqueous solutions of 3d metals. In order to prevent the formation of insoluble sulfides, the reactions of Zn(II) and Mn(II) with [MS₄]²⁻ have been investigated in this work in the presence of ammonia and two organic diamines (en) or (1,2-pn). The reaction of Zn(II) or Mn(II) with [MS₄]²⁻ in 1:1 mole ratio with excess ammonia results in the formation of the tetrammine zinc(II) compounds [Zn(NH₃)₄][MS₄] (M = Mo(2); W (2a)) while a hexamine manganese (II) is the charge balancing cation in [Mn(NH₃)₆][MS₄] (M = Mo(5); W (5a)). In contrast, for the reactions of Zn(II) or Mn(II) with [MS₄]²⁻ in 1:1 mole ratio in the presence of en or 1,2-pn

resulted in the formation of tetrasulfidometalates charge balanced by the tris(diamine)metal(II) complex cation of the type [M'(L)₃] (M' = Zn or Mn; L = en or 1,2-pn). In view of the facile formation of [M'(en)₃][MS₄] (M' = Zn or Mn) compounds, reactions using a mixture of the bivalent metal ions Zn(II) and Mn(II) with [MS₄]²⁻ were investigated in the presence of en. These reactions afforded the synthesis of Mn doped Zn compounds (1) and (1a) and the presence of Mn(II) in these compounds was confirmed by a characteristic spot test for Mn(II) and characteristic ESR spectra. It is interesting to note that complexes of the type [M'(en)₃][MS₄] (M' = Ni or Mn) have also been obtained under solvothermal conditions¹⁹. It is to be noted that in the presence of aromatic diimines like 2,2'-bipyridine (bpy), or 1,10-phenanthroline (phen), Mn(II) forms S-bridged bimetallic compounds containing the {Mn(μ-S)₂MS₂} unit¹⁸ where the [MS₄]²⁻ functions as a bridging bidentate ligand. The presence of a free uncoordinated [MS₄]²⁻ unit in the compounds (1)-(7) and (1a)-(7a) can be inferred from the colour of the compounds (orange for Mo; yellow for W) and characteristic uv-visible and infrared spectra. All our efforts to prepare S-bridged metal complexes by varying the reaction conditions and changing the stoichiometry of the bivalent metal and [MS₄]²⁻ reagents have not been fruitful and the compounds (1)-(7) and (1a)-(7a) are the only isolable products irrespective of the ratio of bivalent metal (excess) or [MS₄]²⁻ (excess) employed. All the compounds prepared in this work, are analysed satisfactorily and the formulae of the compounds was arrived at based on elemental analytical data (Supplementary data Table S2). The compounds are insoluble in water and common organic solvents and dissolve in DMF or DMSO. The compounds are not stable in acid as evidenced by the formation of insoluble trisulfide MS₃ with evolution of H₂S on reaction with dilute HCl. The acid decomposition reaction using excess H⁺ thus provides a convenient method for the estimation of the bivalent metal content, which can be determined after filtering off the insoluble MS₃.

B. Spectral studies

A combination of IR, UV-visible and ESR has been employed to characterize the synthesised complexes. The electronic spectra of the synthesized compounds (1)-(7) and (1a)-(7a) exhibit characteristic bands in the UV-Vis region (Supplementary data Table S4) and the observed signals can be assigned for the intraligand charge transfer transitions of the tetrahedral [MS₄]²⁻ chromophore¹⁷ (Supplementary Data Fig S5).

The infrared (IR) spectra of the synthesized compounds containing en or 1,2-pn exhibit several sharp bands in the mid-infrared region indicating the presence of the organic moieties ethane 1,2-diamine and propane 1,2-diamine (Supplementary data Table S3).

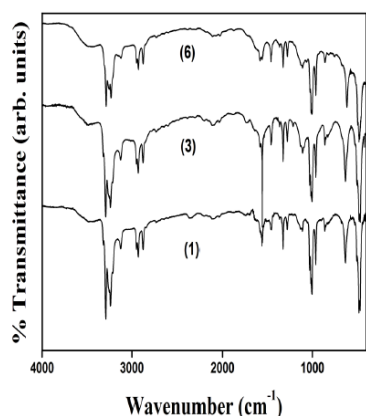


Fig.1 Comparative infrared spectra of [Zn(en)₃][MoS₄] (3), [Mn(en)₃][MoS₄] (5) and Mn doped [Zn(en)₃][MoS₄] (1).

All compounds exhibit an intense absorption peaks in the lower energy region assignable for the asymmetric stretching ν M-S vibration in the free tetrasulfidometalate. This occurs at around ~ 480 cm^{-1} and ~ 460 cm^{-1} in [MoS₄]²⁻ and [WS₄]²⁻ compounds respectively. The intense band in the region around 3100-3300 cm^{-1} can be attributed to N-H symmetric and asymmetric stretching frequency of ammonia or organic diamine. The sharp peaks in the region 1300-1600 cm^{-1} occur due to the symmetric and asymmetric N-H bending vibrations. These vibrations are lowered in the region 1110 - 1250 cm^{-1} in case of ammonia complexes. The intense band around 650-750 cm^{-1} in all the complexes is due to N-H rocking vibrations. In the complexes (1), (1a), (3), (3a), (4), (4a), (6), (6a), (7), (7a), a strong band is observed around 1004 cm^{-1} assignable to the C-N stretching. The prominent bands in the region 2900-2800 cm^{-1} have been assigned due to asymmetric and symmetric C-H stretching and bands around 1350-1460 cm^{-1} are assigned to symmetric and asymmetric CH₂ bending vibrations²³. In complexes (4), (4a) and (7), (7a), symmetric and asymmetric CH₃ bending vibrations are also observed in the region 1370-1460 cm^{-1} (Supplementary data Table S3). The infrared spectrum of [Zn(NH₃)₄][MoS₄] differs from that of the [Mn(NH₃)₆][MoS₄] (Fig.1), which can be explained due to the differing coordination (4 for Zn; 6 for Mn) of the bivalent metal. The IR spectra of the [M'(en)₃][MS₄] (M = Mo, W; M' = Mn, Zn) complexes (Fig.1) are very similar indicating these compounds have similar structure and no change is observed by changing the bivalent metal. Similar pattern is observed for [M'(1,2-pn)₃][MS₄] (M = Mo, W; M' = Mn, Zn) complexes (Supplementary data Fig S7). The crystalline nature of these compounds was also inferred from their X-ray powder pattern (Supplementary data Fig. S18). It is to be noted that the infrared spectra of the [M'(en)₃][MoS₄] (M' = Mn, Zn) compounds and Mn doped [Zn(en)₃][MoS₄] (M=Mo, W) are almost identical in nature (Fig.1) but are different from the previously reported²⁰ spectrum of (enH₂)[MoS₄], which can be attributed to the differing nature of the counter cations. The Zn(II) compounds are diamagnetic while the Mn(II) compounds are paramagnetic and hence were studied by ESR spectroscopy. The esr spectrum of a paramagnetic substance is generally determined by operating at a fixed frequency and varying the field strength. In pure paramagnetic solids the spin-spin interaction between neighbouring magnetic dipoles causes the esr signal to be broadened. This broadening can be

minimised by increasing the distance between the interacting dipoles. For this reason esr spectra are determined by using a paramagnetic material dissolved in large amount of diamagnetic solids. In view of this, paramagnetic Mn (II) has been doped in an isomorphous host complex [Zn(en)₃][MoS₄]. The ground state for Mn(II) in these complexes is found to be 6S_{5/2}. All the Mn compounds (5-7; 5a-7a) described in this work exhibit a single broad signal with a g value ~ 2 (Supplementary data table S13, S14) in their ESR spectra at room temperature. The observed feature can be attributed to dipolar broadening as the spectra of pure polycrystalline (magnetically concentrated) samples were investigated. The ESR spectrum of [Mn(en)₃][MoS₄] (6) is shown in (Fig.2).

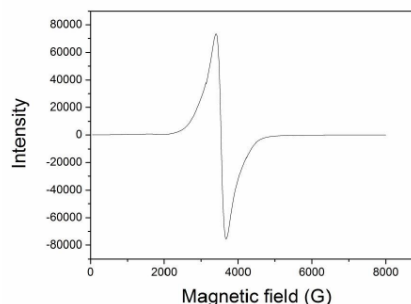


Fig.2 First derivative ESR spectrum of polycrystalline [Mn(en)₃][MoS₄] (6)

This observation is very similar to the reported ESR spectra of [(bpy)₂MnS₂MS₂] compounds¹⁸ which exhibit g values close to the free electron value. Unlike compounds (5-7) and (5a-7a), the Mn doped Zn compound (1,1a) exhibits a six line hyperfine spectrum (Fig.3). The observed A value of 86 gauss is in agreement with reported data¹⁸. The observation of a hyperfine ESR spectrum indicates that magnetic dilution has been achieved in solid state by doping Mn in the diamagnetic Zn(II) complex.

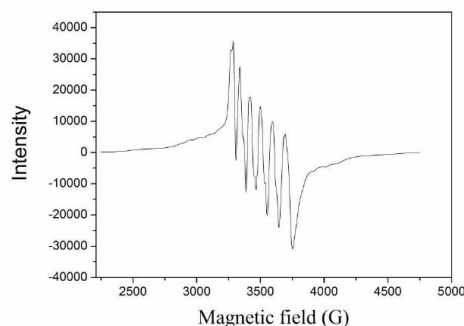


Fig.3 First derivative ESR spectrum of Mn doped [Zn(en)₃][MoS₄] (1)

C. Thermal studies

It is well documented that organic ammonium tetrasulfidometalates are useful precursors for sulphide materials (MS₂) which can be prepared by thermal decomposition²¹. Hence the thermal decomposition studies of these complexes were investigated. The TG analysis of (2) showed two major mass loss steps between 150 oC -200 oC and 200 oC -400 oC.

The mass loss associated with this step is 18% in reasonable agreement with the % mass loss expected 19% indicative of the loss of four ammonia molecules (Supplementary data Fig. S15). The probable solid after, ligand loss would be MMS_4 , ie $MS.MoS_3$. MoS_3 has been reported to decompose to MoS_2 and S at 310 oC 24 and the boiling point of S is 440 oC 25. In view of this the second mass loss step in (2) is attributed to the conversion of MoS_3 to MoS_2 and S19. The W analogue undergoes the similar trend. TG pattern for compound (5) differs from (2) and could be attributed to its hexacoordinate nature, % mass loss in the first step is 27.9 in agreement with the % mass loss of 26.8 for six molecules of ammonia which are lost in the region 100 oC -400 oC. This observation is consistent with the IR pattern of decomposed complexes (2), (2a), (5), (5a) at 200oC (supplementary data Fig. S8). Based on the featureless IR spectrum above 400 oC for these complexes the decomposed products can be formulated as $[M'S.MS_3]$.

It has been observed in the complexes (3), (3a), (4), (4a), (6), (6a), (7), (7a) that the coordinated diamine is lost in two steps. In the first step the mass loss approximately corresponds to two diamines in the range 200 oC -400 oC giving rise to phase $[M'enMoS_4]$ which exhibits an infrared spectrum (Supplementary Data Fig. S16, Fig.17) similar to that of the catena -M-ethylenediamine complex $[M(en)Cl_2]_{22}$. Subsequently followed by the loss of third coordinated diamine above 400 oC. This ultimately results in the formation of mixed metal sulphides in the second step. This observation is also supported by the presence of characteristic N-H and C-H vibrations in the IR spectra of the decomposed products at 200 oC (supplementary data fig S9, fig.S10) and 400 oC (supplementary data Fig. S11, Fig.S12). This study is consistent with the mass loss data (table 1).

Table 1. Thermal analysis data for decomposition of complexes in N₂ atmosphere

compound	Temp range °C	Experimental weight loss %	Probable products	solid weight loss%	DTA peak
[Zn(NH ₃) ₆]MoS ₄	150-200	18.00	ZnSMoS ₃	19.02	145 endo
					4210 exo
[Mn(NH ₃) ₆]MoS ₄	100-400	27.86	MnSMoS ₃	26.77	100 exo
					390 exo
[Zn(en)]MoS ₄	150-370	25.97	Zn(en)MoS ₄	25.56	200 endo
	450-510	36.00	ZnSMoS ₃	38.34	485 endo
[Zn(en)]WS ₄	200-400	20.80	Zn(en)WS ₄	21.52	200 endo
	400-600		ZnSMoS ₃	32.30	475 endo
[Mn(1,2-pn)]MoS ₄	200-400	32.58	Mn(1,2pn)MoS ₄	30.00	170 exo
	200-600		MnSMoS ₃	44.31	600 exo
[Mn(1,2-pn)]WS ₄	200-470	26.00	Mn(1,2pn)WS ₄	25.13	170 exo
	200-800	36.00	MnSMoS ₃	38.00	480 exo

IV. CONCLUSIONS

The present work describes a methodology for the facile synthesis of complexes obtained by reaction of cationic salts charge balanced by $(MS_4)_2$ anions of the formula $[M'(L)_n][MS_4]$ ($M' = Zn(II)$ and $Mn(II)$; $L = NH_3$ or en or $1,2-pn$; $M = Mo$ or W). The complexes thus prepared have been characterized by analytical data, thermal, uv-visible, ESR and infrared spectra. The $Mn(II)$ compounds exhibit broad ESR signals while the magnetically diluted (Mn -doped) $Zn(II)$ compound exhibits a hyperfine spectrum. The thermal studies of these complexes provides easy route to their characterization as the ammonia and diamines are lost at particular temperature and the decomposition products are the mixed metal sulphides which are the potential materials and

next generation catalysts.

Supplementary Data

Supplementary Data associated with this article are available in the electronic form at <http://www.niscair.res.in/jinfo/ijca/IJCA> 51A(XX) YYYY-YYYY_Suppl Data.pdf

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