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Characterization of Thin Films of Mixed Complexes of Rare Earth, Mo and W ions

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Abstract: ***The structure of new compound of the type $[Pr(SH)\ (OH)\ _2H_2O]$ has already been established in our earlier publication (JCGCM 2002). When aqueous solution of ammonium molybdate $[NH_4)_2\ MoO_4\ 2H_2O]$ was mixed with $Na_2S\ 7H_2O$, yielded yellow solution due to reducing nature of sodium sulfide. Yellow solution, $(NH_4)_2\ [MoO_2(H_2O)_2\ ]$ was mixed with green solution of the compound, $[Pr(SH)(OH)_2H_2O]$, a brownish red color solution $[MoO_2\ (H_2O)_2\ Pr(SH)\ (OH)_2\ H_2O\ ]^{2-}[NH_4]^{2+}$ was obtained which showed $\delta \rightarrow \delta$ transition at 500 nm, intervalence $Pr^{3+} \rightarrow Mo^{4+}$ band at 425 nm and a steep broad band from 850 to 950 nm due to H- bonding. When aqueous solution $(NH_4)\ _2[\ WO_4\ 2H_2O\ ]$ was mixed with the compound $[Pr(SH)\ (OH)_2\ H_2O\ ]$ a green color solution $[\ WO_2\ (H_2O)_2\ Pr(SH)\ (OH)_2\ H_2O]^{2-}$ was obtained which showed intervalence $Pr^{3+} \rightarrow W^{3+}$ band at 500 nm. On addition of an inert solvent CCl_4, the steep broad band at 850-950 nm due to H- bonding disappeared, ascertaining the polymeric nature due to H- bonding of the compound. The structure of thin film of solutions was established by XRD pattern, IR spectra, SEM and TEM showed nearly spherical grains having average size 50-100 nm.***

Keyword: Polymeric nature, spherical grains, XRD pattern, SEM and TEM

1. Introduction

Acidic solutions of ammonium molybdate and ammonium tungstate form polymeric [1] anions below 6 pH [2]. It is reported that hot solutions of oxide hydrate $[NH_4)\ _2\ Mo\ O_4\ 2H_2O]$ contain sheets of MoO_6 octahedra with one H_2O bound to MO, the other water molecule is hydrogen bonded in the lattice [1]. Further it is reported that on addition of small cation to anion, $[Mo_2O_7\ ]^{-2}$, it is converted to polymeric anion $[Mo_7O_{24}]^{-6}$. MoS_2 occur in nature as molybdenite [1]. Structure of MoS_2 (having lubricating property) consists of layers of sulfide ions, a metal ion layer and then another sulphide ion layer [3-9]. MoS_2 has closed packed layers of sulfur atoms stacked to create trigonal prismatic interstices that are occupied by Mo atoms. WS_2 has similar structure. Intercalation compounds [4] do show interesting properties. The formation of heteropoly $[Co_2W_{11}O_{40}H_2]$ anions has also been reported [1]. Intense red colored compound $[\ Mo_2Cl_6]^{-4}$ shows δ - δ* transition [1,10] at 525 nm due to quadruply bonded (Mo ≣ Mo)species having excitation of electron from a singlet → singlet, triplet → triplet state [1] and has clustering nature. Luck and Morris [1] have discovered Mo ≣ W bond which has been utilized by Cotton and James [7]. The synthesis of hetropoly thio anion remains open to further investigation. Therefore synthesis and characterization of mixed complexes of rare earth, Mo and W system has been investigated in present paper.

2. Experimental

The compounds of praseodymium and neodymium ions were prepared by mixing aqueous solutions of Na_2S with solution of $PrCl_3$ (green) and $NdCl_3$ (purple) in 1:1 molar ratio. When aqueous solution of ammonium molybdate, $(NH_4)\ _2Mo\ O_4\ 2H_2O$ was mixed with $Na_2S\ 7H_2O$ yielded yellow solution, $(NH_4)\ _2MoO_2\ (H_2O)\ _2$, along with solid sulfur due to reducing nature of sodium sulfide. After filtering yellow solution, $(NH_4)\ _2MoO_2\ (H_2O)\ _2$ was mixed with the compound $[Pr(SH)(OH)_2H_2O]$ a brownish red colour solution, $[MoO_2\ (H_2O)Pr(SH)(OH)\ _2\ H_2O]^{2-}\ [NH4]^{2+}$, was obtained. Similarly the compound of W ions was synthesized by mixing aqueous solutions of Na_2S7H_2O with ammonium tungstate. When the compound of Pr^{3+} ion was mixed with solution of Mo^{4+} ion it resulted in a transparent reddish brown colour solution which is stable. Similarly the compounds of Pr^{3+} ion mixed with solution of W^{4+} ion resulted in a transparent green colour solution. Thin films of these solutions of the complexes were grown for one month and annealed above 400 ^{0}C. IR spectra of solutions were run in the range 4000 cm $^{1-}$ to 400 cm^{1-} using polythene container on a Perkin FT-IR spectrophotometer RX- IB UK. The X-ray powder diffraction of thin films of solutions were carried on RIGAKU-Rota – Flex RAD/ Max-B, Rigaku, corporation, Japan, X-ray Diffractometer using Cu K radiation with $2\theta = 5 - 80^0$ with scanning speed of 1^0 per minute. Electronic spectrum of solutions of the complexes was recorded on a Shimadzu 160A Spectrophotometer in water (10^{2-} m molar). SEM photograph has been produced from Scanning Electron Microscope, JEOL-840, JEOL corporation Japan. TEM photographs have been produced from Transmission Electron Microscope, JEOL 2000 EX JEOL, corporation, Japan. The films were cut in appropriate size (10 mm approx.) and coated with gold to avoid charge accumulation on the surface of film.

3. Result and Discussion

The crystal structure and physicochemical properties of complex, $[Pr(SH)(OH)_2\ H_2O]$ have been reported in our publication [11]. Hydroxy compounds in pure liquid state exist as polymeric aggregates held together by hydrogen bonds which break [12] on dilution with nonpolar solvents first to trimer and finally to monomer. Aqueous solution of ammonium thiomolybdate $(NH4)_2MoS_4$ on heating, yielded cationic complex $[Mo_4S_4\ (H_2O)_{12}]^{n+}$ with octahedral site of molybdenum at diagonal sites of faces of cubic lattice. Charge transfer bands may occur at 204nm due to Na_2S $[3S^23P^63d^0(S-2)]$ $4f^2(Pr^{3+}ion)$. In reddish brown complex, $[MoO_2\ (H_2O)_2Pr(SH)(OH)_2\ H_2O]^{2-}[NH4]^{2+}$, the peaks of reactants Na_2S (305nm), $PrCl_3$ at 193, 214 nm and $(NH_4)2MoO_4\ 2H_2O$ at 323nm disappeared and peaks at 204nm (sharp), 250, 380,450nm (sharp) and 856-900nm (w,broad) appeared due to charge transfer bands, f-f transition $({}^3H_4 - {}^3P_0, {}^3P_1, {}^3P_2)$ (Table-1) and H - bonding(Fig.-2a). Intense red colour of $[Mo_2Cl_6]^{4-}$ shows δ - δ* transition [1] at 525nm due to quadruply bonded (Mo ≣ Mo) species having excitation of electron from a singlet → singlet state [1] or triplet → triplet state and clustering nature. Most probably the red colour of the complex is due to δ - δ* transition at 500nm and intervalence [1,2] f – d transition, Pr^{3+} ≣ Mo^{4+} at 425 nm, ascertains $(4f^2)\ Pr^{3+}$ - $(4d^2)Mo^{4+}$ bonds[7] in our compounds. The band due to H-bonding at 865-900nm disappeared when UV Visible spectrum was taken in CCl_4 nonpolar solvent (Fig.2b). Hydrogen bonds which break upon dilution with nonpolar solvent have been reported [2]. The UV Visible spectrum of H_2O (which has H- bonding) shows band at 1000nm (Fig.4). In green colour solution of the complex, $[WO_2\ H_2O\ Pr(SH)(OH)_2\ H_2O]^{2+}$ the band at 370nm of $Na_2WO_4\ 2H_2O$ splits to 400 (25000 cm^{-1}), 490 (166000 cm^{-1}) nm on complexation due to sharp strong charge transfer band and strong sharp f-f transition respectively (Fig.3a,3b). δ - δ* transition at 500nm as shoulder imparts green colour to the complex which is most probably masked, ascertains $(4f^2)Pr^{3+}$ - $(5d^2)W^{4+}$ bond. A broad weak band at 690-900, 1100nm might be due to H-bonding in green colour solution of the complex [7-13]. The structure of thin film of solutions were established by XRD pattern, IR spectra, SEM (Fig.-5) and and TEM (Fig.-6) of film of solutions showed nearly spherical grains having average size 50-100 nm.

On the basis of above facts tentative structure of heteropoly thio anion complex [14-17] in presence of reducing species Na_2S can be suggested.

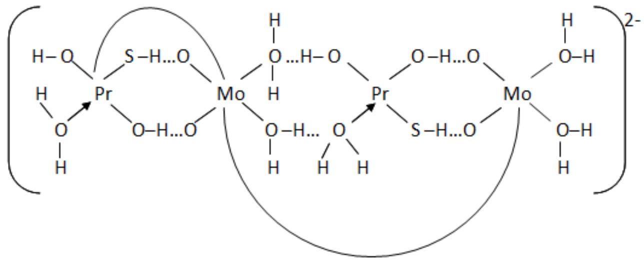

Figure 1: Structure of the complex $[MoO_2(H_2O)Pr(SH)(OH)_2H_2O]^{2-}$ anion

X-ray powder diffraction pattern of thin film of compound, $[MoO_2(H_2O)\ Pr\ (SH)\ (OH)_2H_2O]^{2-}\ [NH_4]^{2+}$ has hexagonal crystal structure (Table-2). The IR spectra of solutions of both the complexes show shifting in frequencies with respect to parent compound $[Pr\ (SH)(OH)_2(H_2O)]$. IR spectrum of parent compound show medium band at 2361 cm^{-1} due to H-bonding as O-H…O. vibrational modes appear at 3640, 3339 cm^{-1}, 2134.88 cm^{-1} and 1940 cm^{-1} due to νOH(H_2O) νSH and νOH respectively (Table-3). In finger print region bending mode of vibration due to H_2O do appear at 1645 cm^{-1} Td symmetry [18-23] vibration modes at 1250, 1145, 1000, 900 and 800 cm^{-1} also appear. There are bands at 870, 780, 760, 600, 550, and 500 cm^{-1} due to νMo-O, ν W-O, νPr-O and νMo-S, νW-S, νPr-S respectively.

4. Conclusion

Heteropoly thio anion complex, $[MoO_2(H_2O)_2Pr(SH)(OH)_2H_2O]^{2-}$ with H-bonding shows special structure which explores the possibility of intervalence f- d transition at 425 nm, ascertains $(4f^2)\ Pr^{3+}$ - $(4d^2)\ Mo^{4+}$bond δ - δ* transition at 525nm due to quadruply bonded (Mo ≣ Mo) species.

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Table 1: Electronic spectral bands and bonding parameters of $[MoO_2(H_2O)_2Pr(OH)_2(SH)(H_2O)]^{2-}[NH_4]^{2+}$ Compound

Complex	Band (cm-1)	S'L' J'	Spectral Parameter
Pr - Mo	20000 21276 22471 11488(880nm) Due to H- bonding	$^3P_0$ $^3P_1$ $^3P_2$	β=0.7908 9 More covalence) $b^{1/2}$= 0.3324 δ%= 0.282 η=0.0016
Ground state of Pr(III) is $^3H_4$			

Table 2: XRD Pattern of thin film of $MoO_2(H_2O)_2Pr(OH)_2(SH)(H_2O)]^{2-}[NH_4]^{2+}$ Compound

θ	*Sin θ*	*Sin² θ*	*d (A⁰)*	*I/I₀*	*(h k I)*
0.0045	0.13925	0.01939	5.5316	50.0	
9.2355	0.16049	0.025725	4.7994	100.0	
9.4365	0.16395	0.02688	4.6981	87.5	
9.6025	0.16681	0.02826	4.6177	75.0	
10.9295	0.18960	0.03594	4.0626	100.0	(001,cubic), (100,tetra)
11.8960	0.20613	0.04249	3.7368	62.5	(002,hexa)
13.4020	0.23178	0.05372	3.3233	62.5	(002,hexa)
13.8915	0.24008	0.05764	3.2084	100.0	(002,hexa)
29.8040	0.49718	0.24719	1.5498	62.5	(201,tetra)

XRD Pattern of thin film of $[WO_2(H_2O)_2Pr(OH)_2(SH)(H_2O)]^{2-}$ $[NH_4]^{2+}$ Compound is also hexagonal.

Table 3: IR Spectra of $[MO_2(H_2O)_2Pr(OH)_2(SH)(H_2O)]^{2-}$ $[NH_4]^{2+}$ [M = Mo,W]

Mo-Pr	W-Pr	Assignment
Red Brown Soln.	Green Soln.	νH_2O sym broad, str H-O-H H,bond
3640.17-2800 cm-1	3339.90 ν broad cm-1	
2134.88	2134.88 m, str	ν SH
1940.43 cm-1	1940.43 M, str	ν OH
1641.5		δ H_2O
1645.86		----
1125		Td sym
999		
930.940		ν Mo—O
864		
700		
495		
450		ν Ln-----O
485		ν Ln----S, Mo---S

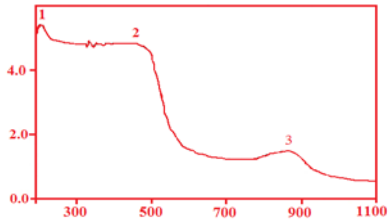

Figure-2a UV-Visible Spectrum of compound of $[MoO_2(H_2O)_2Pr(OH)_2(SH)(H_2O)]^{2-}$

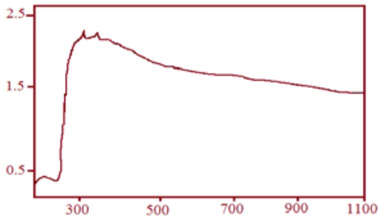

Figure-2b UV-Visible Spectrum of compound of $[MoO_2(H_2O)_2Pr(OH)_2(SH)(H_2O)]^{2-}[NH_4]^{2+}$ in CCl_4

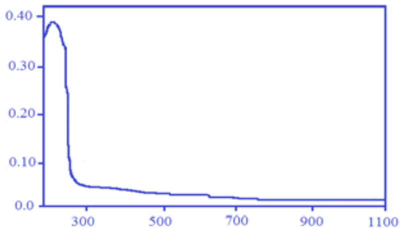

Figure-3a UV-Visible Spectrum of compound of $[WO_2(H_2O)_2Pr(OH)_2(SH)(H_2O)]^{2-}$ $[NH_4]^{2+}$

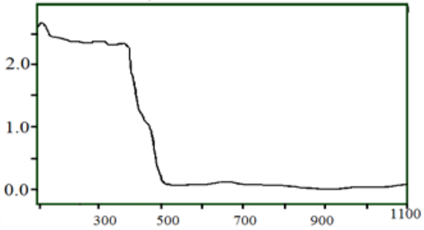

Figure-3b UV-Visible Spectrum of compound of $[WO_2(H_2O)_2Pr(OH)_2(SH)(H_2O)]^{2-}$ $[NH_4]^{2+}$ in CCl_4

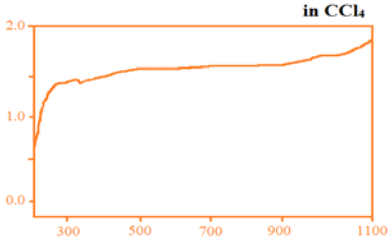

Figure- 4. UV-Visible Spectrum of H_2O

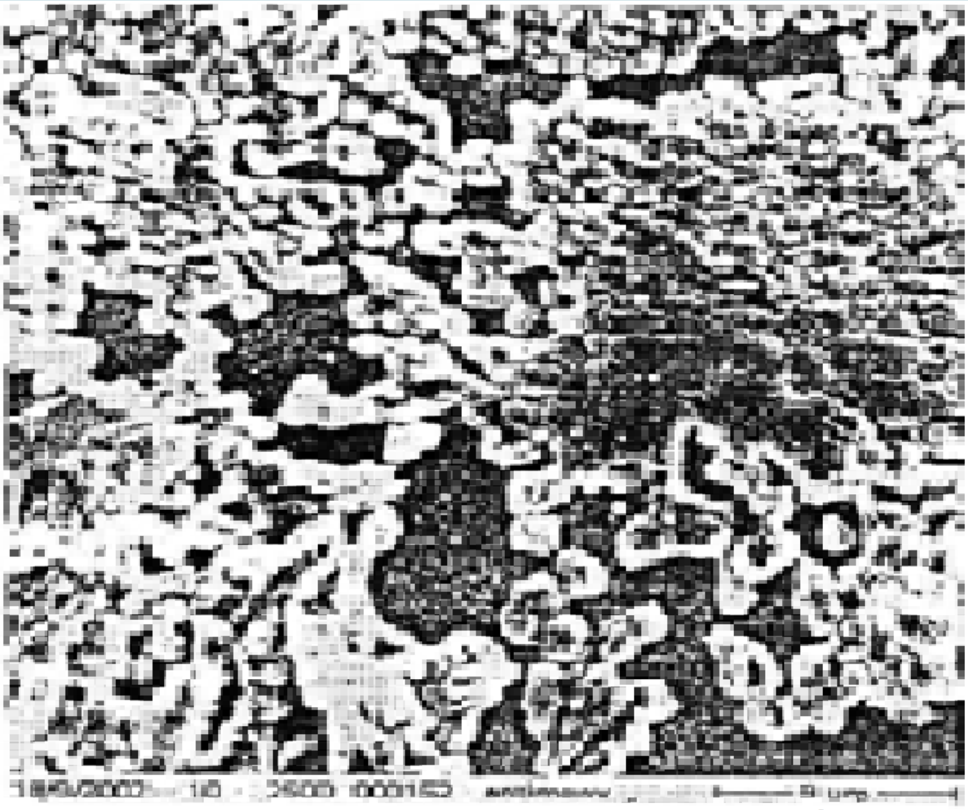

Figure-5. SEM of thin film of compound of $[MoO_2(H_2O)_2Pr(OH)_2(SH)(H_2O)]^{2-}[NH_4]^{2+}$

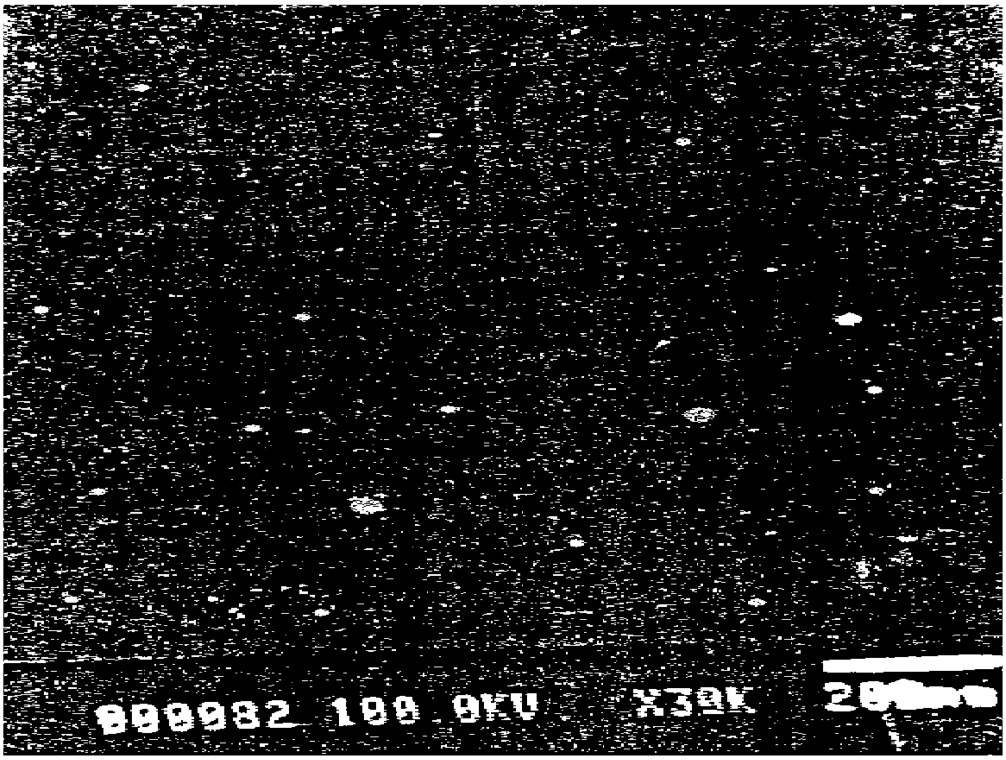

Figure-6. TEM of thin film of compound of $[MoO_2(H_2O)_2Pr(OH)_2(SH)(H_2O)]^{2-}[NH_4]^{2+}$