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Mixed metal Fe-Mo complexes with schiff bases of triethylenetetramine & diethylenetriamine

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ABSTRACT

Mixed metal complexes of Fe(III) and tetrathiomolybdate have been synthesized with Schiff bases of triethylenetetramine (trien)/ diethylenetriamine (dien) formed from acetophenone and acetylacetone. The complexes are characterized by elemental and thermal analysis, IR, UV-Visible spectral studies, magnetic and EPR studies. The complexes probably have a structure containing $FeMoS_4$ cluster with ferric iron linked to a chloro ligand and two or four $CH=N$ nitrogens of the trien/dien based Schiff bases. The complexes have a composition [(trien-4H) $(CCH_3C_6H_5)_2 (FeMoS_4) Cl$]. H_2O and [(dien-4H) $(CCH_3C_6H_5)_2 (FeMoS_4) Cl (H_2O)$] and [(dien-4H) $(CH_3CCH_2CCH_3)_2 FeMoS_4.Cl$] and [(trien-4H) $(CH_3CCH_2CCH_3) FeMoS_4.Cl$]. $6H_2O$. The acetophenone Schiff base complexes of trien and dien show promising antibacterial activity against *Bacillus cereus* and *Bacillus subtilis*.

Key Words: Ferric tetrathiomolybdate, triethylenetetramine / diethylenetriamine Schiff base, Mixed metal Ferric - Molybdenum complex, antibacterial studies.

INTRODUCTION

Interaction of tetrathiomolybdate with iron is an important reaction having biorelevance, with respect to nitrogenase enzyme [1-3]. The biological nitrogen fixation amounts to about 1.2×10^8 tons of nitrogen fixed per year. In contrast to this hundreds of chemical plants throughout the world produce about 10^3 tons of ammonia per day i.e., 3.65×10^5 tons of ammonia per year through the Haber Bosch's process employing drastic conditions of temperature and pressure. Chemists have basic interest in synthesizing iron-molybdenum and several metal clusters which

may help in invitro nitrogen fixation [4-7]. Here we report bimetallic trien / dien based Schiff base complexes with Ferric iron and tetrathiomolybdate.

EXPERIMENTAL SECTION

All reagents used were of analytical grade and used without purification. 1 mole of Trien / dien and 2 moles of acetophenone are added simultaneously to an aqueous solution of 1 mole of ferric chloride and stirred well for ten minutes. Schiff base complex is formed. To this added tetrathiomolybdate prepared from ammonium heptamolybdate of 0.14 mole by passing H₂S for 3 hrs, and removing the mother liquor. The mixture is stirred continuously for about an hour when the complex is obtained as a dark brown mass. For the acetylacetone complex 1 mole of trien / dien and acetylacetone are added to 1 mole / 0.5 mole of ferric chloride aqueous solution for trien and dien complexes respectively and stirred well for ten minutes. To the Schiff base complexes formed added tetrathiomolybdate prepared from 0.14 / 0.07 mole of ammonium heptamolybdate for the trien and dien complexes respectively. The mixture is stirred for about an hour and the complex is separated. The complexes are washed with water-alcohol mixture and dried in air. Iron and Molybdenum in the complex were determined by optical emission spectroscopy using ICP-OES Perkin Elmer optima 5300 DV Spectrometer and Nitrogen is estimated by Kjeldhal's method. Sulphur in the complexes was analyzed gravimetrically as BaSO₄. TG/DTA were recorded in nitrogen atmosphere using NETZSCH STA 409 C/CD thermal analyzer with a heating rate of 10°C/min. Magnetic susceptibility studies were carried out using vibrating magnetometer EG and GPARC model 155. UV-Visible absorption spectra were recorded in DMSO using Varian Cary Spectrophotometer 5E-UV-Vis-NIR. IR spectra were recorded in KBr using Bruker IFS 66V FT IR spectrometer. Conductivity of the complexes in DMSO was measured using simple conductivity bridge. Anti bacterial activity of the complexes was tested using minimum modification of the disc diffusion method[8].

RESULTS AND DISCUSSION

The elemental and thermal analysis data (Table I & II) indicated the composition to be [(trien-4H) (CCH₃C₆H₅)₂ (FeMoS₄) Cl] · H₂O and [(dien-4H) (CCH₃C₆H₅)₂ (FeMoS₄) Cl (H₂O)] for the acetophenone complexes and [(trien-4H) (CH₃CCH₂CCH₃)₂ FeMoS₄. Cl] · 6H₂O [(dien-4H)(CH₃CCH₂CCH₃)₂ FeMoS₄.Cl] for acetyl acetone complexes. The complexes are highly soluble in DMSO, insoluble in alcohol and CHCl₃. TG and DTA data (Table II) indicates that the trien complexes and dien acetophenone complex lose water molecules from 50°C onwards indicates less thermal stability. Water of hydration in trien complexes is also indicated with an endotherm in DTA while the acetophenone dien complex shows an exotherm at +91.3°C perhaps indicating that water could be a coordinated water. However loss of water is not a discrete step. Further loss leads to the final product FeMoS₄O_{0.5}. The decomposition are marked by number of exothermic and endothermic peaks in DTA curves. The molar conductance of the complexes in DMSO range around 10-30 ohm⁻¹ cm² mole⁻¹ indicating non electrolytic nature.

Table – I The elemental analysis and electronic spectral data on the complexes

COMPLEXES	%Fe	%Mo	%N	%S	%Cl	Λ_{\max} (nm)
	EXP (THEO)	EXP (THEO)	EXP (THEO)	EXP (THEO)	EXP (THEO)	
[(dien-4H)(CCH ₃ C ₆ H ₅) ₂ (FeMoS ₄)Cl(H ₂ O)]	9.21 (8.72)	15.21 (14.98)	6.02 (6.55)	20.9 (19.99)	5.21 (5.53)	288, 362.5, 481.8
[(dien-4H) ₂ (CH ₃ CCH ₂ CCH ₃) ₂ (FeMoS ₄)Cl]	8.92 (8.60)	15.30 (14.70)	11.92 (12.93)	19.02 (19.71)	5.02 (5.46)	263.5, 317.8, 476.7
[(trien-4H)(CCH ₃ C ₆ H ₅) ₂ (FeMoS ₄)Cl].2H ₂ O	8.23 (7.96)	14.56 (13.68)	8.01 (7.98)	18.12 (18.23)	6.22 (5.05)	278.2, 315.8, 407.05 475.2
[(trien-4H)(CH ₃ CCH ₂ CCH ₃)(FeMoS ₄)Cl].6H ₂ O	9.25 (8.81)	16.24 (15.15)	9.63 (8.84)	20.05 (20.18)	6.54 (5.59)	292.3, 315.8, 463.45

Table-II TGA and DTA data ON Cu-Mo complexes

COMPLEXES	% Residue EXP (THEO)	DTA peaks corresponding to water loss	DTA peaks corresponding to ligand decomposition °C
[(dien-4H) (CCH ₃ C ₆ H ₅) ₂ (FeMoS ₄)Cl(H ₂ O)]	44.0 (44.9)	+91.3	+541.1, +653, +1023.9
[(dien-4H) ₂ (CH ₃ CCH ₂ CCH ₃) ₂ (FeMoS ₄)Cl]	44.3 (48.0)	-	+107.1, +421, +1151.7
[(trien-4H)(CCH ₃ C ₆ H ₅) ₂ (FeMoS ₄)Cl].2H ₂ O	42.0 (41.04)	(-)38.5	-121, +489.1,+1035.6,-1115.2
[(trien-4H)(CH ₃ CCH ₂ CCH ₃)(FeMoS ₄)Cl].6H ₂ O	45.0 (45.44)	(-)38.5	+91.9,+166.1,+793.5

The magnetic susceptibilities of the complexes indicated the presence of one unpaired electron per molecule corresponding to low spin ferric iron ($t_{2g}^5 e_g^0$) and molybdenum(VI). The complexes show absorbance in the region 405-485nm corresponding to low spin ferric iron in octahedral environment [9]. The absorbance below 400 nm corresponds to S-Mo charge transfer [10]. IR spectra of the complexes (Table-III) indicate a broad band in the region 3385-3580 cm^{-1} corresponding ν_{OH} and ν_{NH} and $\nu_{\text{C=N}}$ of the Schiff base and $\nu_{\text{C=C}}$ of the phenyl ring could not be distinctly assigned and appear in the region 1405-1640 cm^{-1} . The complexes show bands in the region 920-950 cm^{-1} and 529-555 cm^{-1} corresponding to $\nu_{\text{Mo=S}}$ and $\nu_{\text{Mo-S}}$ stretching respectively.

Table – III IR spectral data on complexes (wave numbers cm^{-1})

COMPLEXES	ν_{NH} , ν_{OH}	$\nu_{\text{C=N}}$, $\nu_{\text{C=C}}$	$\nu_{\text{Mo=S}}$	$\nu_{\text{Mo-S}}$
[(dien-4H)(CCH ₃ C ₆ H ₅) ₂ (FeMoS ₄)Cl(H ₂ O)]	3434	1618 1448	920 945	532
[(dien-4H) ₂ (CH ₃ CCH ₂ CCH ₃) ₂ (FeMoS ₄)Cl]	3429	1618 1545 1406	935	529
[(trien-4H)(CCH ₃ C ₆ H ₅) ₂ (FeMoS ₄)Cl].2H ₂ O	3389	1628 1592	942	555
[(trien-4H)(CH ₃ CCH ₂ CCH ₃)(FeMoS ₄)Cl].6H ₂ O	3529	1640 1521	950	555

Based on the above discussions the acetophenone complexes are assigned the structure with iron coordinated with two sulphur of tetrathiomolybdate on it and two CH=N nitrogens of the Schiff base. The fifth coordination site of iron is satisfied by the chloro ligand. In the dien complex H₂O is coordinated to the metal while it remains as water of hydration in the trien complex. In the complexes with acetyl acetone based Schiff base coordination occurs through four CH=N nitrogen in the dien complex and two CH=N nitrogens and two NH nitrogens in the trien complex. The fifth coordination site of iron is satisfied by chloro ligand and two sulphur of the tetrathiomolybdate are linked to the ferric iron making a distorted octahedral environment around iron.

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