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### Bimetallic Vanadium-Molybdenum Complexes of Diethylenetriamine and Triethylenetetraamine based Schiff bases

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#### ABSTRACT

Mixed metal complexes of Vanadium (IV) and tetrathiomolybdate/oxomolybdate have been synthesised with schiff bases of diethylenetriamine (dien)/ triethylenetetraamine (trien) formed from salicylaldehyde/ acetophenone. The complexes have been characterized by elemental and thermal analysis, conductivity and magnetic susceptibility, IR, UV- Visible and EPR spectral studies. The complexes probably have a structure containing  $VOMoS_4$ /  $VOMoO_4$  unit with vanadyl moiety linked to two  $CH=N$  nitrogens of the trien/dien based Schiff bases. The complexes have a general formula as  $[(L-4H) (CHC_6H_4OH)_2 VOMoX_4].MH_2O$  where L- dien or trien, X- O or S, M- 6 or 10. L-4H represents L less four hydrogens. The trien- salicylaldehyde complex with tetrathiomolybdate has been found to exhibit promising antibacterial activity against streptococcus aureus and acinetobacter.

**Keywords:** Oxo Vanadium(IV)Tetrathiomolybdate/oxomolybdate, diethylenetriamine /triethylenetetraamine Schiff bases, antibacterial studies.

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## INTRODUCTION

Interaction of tetrathiomolybdate with metal is an important reaction having biorelevance, with respect to nitrogen fixation [1-3]. A system promoting fixation of atmospheric nitrogen gains importance because; it provides nitrogen for plant nutrition, an intriguing process which readily occurs in blue-green algae, azotobacter vinelandii, etc. The biological nitrogen fixation is very important in maintaining the nature's nitrogen cycle. With the increasing consumption of nitrogen fertilizers over the years, hundreds of chemical plants throughout the world are engaged in production of about  $3.65 \times 10^5$  tons of  $\text{NH}_3$  per year through the Haber-Bosch's process [4]. This commercial process of  $\text{N}_2$  fixation requires the drastic conditions like  $450\text{-}600^\circ\text{C}$ , 200-600 atm pressure in addition to the catalysts (based on metallic iron). Several Dinitrogen complexes of vanadium and Molybdenum have been synthesized and converted to nitrogenous products through simple reactions [5-8]. Thus compounds with Mo and V are very important as potential systems for invitro nitrogen fixation. Hence we have synthesized bimetallic vanadium-molybdenum complexes of dien and trien based schiff bases.

## MATERIALS AND METHODS

### EXPERIMENTAL SECTION

All the reagents were of analytical grade and used without purification. Preparation of tetrathiomolybdate involves the reaction between the aqueous solution of ammonium heptamolybdate and  $\text{H}_2\text{S}$  gas for 3 hrs to form dark brown slurry consisting essentially of a solid which is ammonium tetrathiomolybdate. Then the solid is removed from the major portion of the mother liquor. The complexes were prepared by simultaneous addition of dien/trien and salicylaldehyde/acetophenone to aqueous solution of vanadyl sulphate followed by addition of 1 mole equivalent of ammonium tetrathiomolybdate /oxomolybdate. The mixture is stirred well for an hour and the complex is separated. The complexes are washed with water- alcohol mixture and dried in air. Vanadium 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 analysed gravimetrically as  $\text{BaSO}_4$ . TG/DTA were recorded in nitrogen atmosphere using NETZSCHSTA 409 C/CD thermal analyser with a heating rate of  $10^\circ\text{C}/\text{min}$ . Magnetic susceptibility 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. The EPR spectra of the complexes were recorded using varian E-112 electron spin resonance spectrometer in the region from 1000- 8000 gauss. The operating frequency was 930 GHz. Anti bacterial activity of the complexes was tested by disc diffusion method [9].

## RESULTS AND DISCUSSION

TABLE – I ELEMENTAL ANALYSIS AND ELECTRONIC SPECTRA DATA ON THE COMPLEXES

Complexes	% V	% Mo	% n	% S	$\lambda_{(max)}$ (nm)
[(Trien-4H)(CHC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> VO(MoS <sub>4</sub> )].10H <sub>2</sub> O	6.095 (6.17)	12.01 (11.6)	6.62 (6.70)	16.61 (15.5)	279, 312, 381, 485
[(Trien-4H)(CCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> VO(MoS <sub>4</sub> )].6H <sub>2</sub> O	7.29 (6.80)	13.31 (12.8)	7.2 (7.4)	17.98 (17.09)	270, 321, 349, 487
[(Dien-4H)(CHC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> VO(MoS <sub>4</sub> )].10H <sub>2</sub> O	5.12 (6.51)	11.9 (12.2)	4.51 (5.3)	16.87 (16.37)	265, 319, 350, 481
[(Dien-4H)(CCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> VO(MoS <sub>4</sub> )].6H <sub>2</sub> O	7.89 (7.22)	14.51 (13.59)	6.52 (5.94)	17.91 (18.1)	264, 285, 325, 380, 481
[(Trien-4H)(CHC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> VO(MoO <sub>4</sub> )].10H <sub>2</sub> O	6.86 (6.7)	13.81 (12.62)	7.80 (7.36)	--	282, 320, 381
[(Trien-4H)(CCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> VO(MoO <sub>4</sub> )].6H <sub>2</sub> O	7.78 (7.43)	14.38 (14)	7.58 (8.17)	--	280, 302, 382
[(Dien-4H)(CHC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> VO(MoO <sub>4</sub> )].10H <sub>2</sub> O	6.82 (7.1)	14.42 (13.36)	4.98 (5.8)	--	267, 316, 365
[(Dien-4H)(CCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> VO(MoO <sub>4</sub> )].6H <sub>2</sub> O	8.21 (7.93)	14.2 (14.9)	5.92 (6.54)	--	269, 320

TABLE – II TGA , DTG AND DTA DATA ON COMPLEXES

Complexes	% Residue VOMoS <sub>4</sub> / VOMoO <sub>4</sub>	% Residue VMo	DTG Point of inflection(°C)	DTA Peaks water loss °C	DTA Peaks due to decomposition of ligands °C
[(Trien-4H)(CHC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> VO(MoS <sub>4</sub> )].10H <sub>2</sub> O	35.5 (35.26)	18 (17.8)	68,204.1,349.3, 450,938.7	- 100	-300, +389.7, +641.4
[(Trien-4H)(CCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> VO(MoS <sub>4</sub> )].6H <sub>2</sub> O	No discrete step	20 (19.6)	61.8,448.9, 23.6,913	- 69	+151.5,- 473.9,+709.8,+775. 5
[(Dien-4H)(CHC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> VO(MoS <sub>4</sub> )].10H <sub>2</sub> O	36 (37.2)	18.8 (18.78)	74, 235, 370, 547.7, 896, 988.6	-80	+159,+905.1
[(Dien-4H)(CCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> VO(MoS <sub>4</sub> )].6H <sub>2</sub> O	No discrete step	20.2 (20.8)	96.7,277.8,606.5,1 012.2	-70	+142.1,+380.1,+76 7.5,+895
[(Trien-4H)(CHC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> VO(MoO <sub>4</sub> )].10H <sub>2</sub> O	-	20.5 (19.3)	88.9, 322.2, 401.1, 488.8, 913.4	-71.3	-240.5,-306.4,- 402.9,- 495.5,+631.6
[(Trien-4H)(CCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> VO(MoO <sub>4</sub> )].6H <sub>2</sub> O	32.5(33.1)	-	86.0,326.1,440 706.2, 1109.2	-60	+104,+481.5,+675. 1,-1200
[(Dien-4H)(CHC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> VO(MoO <sub>4</sub> )].10H <sub>2</sub> O	-	22 (20.5)	155.3,335.7,507,91 2.7,1230.6	-80	+142.5,-163.4, +500,- 623.4,+1021.9
[(Dien-4H)(CCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> VO(MoO <sub>4</sub> )].6H <sub>2</sub> O	36.0 (35.3)	-	83.4,423.2,580.810 08.1	-70	+147.1,- 437.1,+654,-1200

TABLE- iii IR SPECTRAL DATA ON THE COMPLEXES

Complexes	$\nu_{\text{NH, OH}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C=C}}$	$\nu_{\text{C=N}}$	$\nu_{\text{Mo=S}}$ $\nu_{\text{Mo=O}}$	$\nu_{\text{Mo-S}}$ $\nu_{\text{Mo-O}}$
[(Trien-4H)(CHC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> VO(MoS <sub>4</sub> )].10H <sub>2</sub> O	3422, 3192	2933	1544	1620	941	759
[(Trien-4H)(CCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> VO(MoS <sub>4</sub> )].6H <sub>2</sub> O	3372, 3240	2961	1576	1615	968	769
[(Dien-4H)(CHC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> VO(MoS <sub>4</sub> )].10H <sub>2</sub> O	3413, 3114	2946	1455	1620	931	769
[(Dien-4H)(CCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> VO(MoS <sub>4</sub> )].6H <sub>2</sub> O	3430, 3310	2925	1448	1576	936	803
[(Trien-4H)(CHC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> VO(MoO <sub>4</sub> )].10H <sub>2</sub> O	3420, 3218	2939	1544	1624	879	773
[(Trien-4H)(CCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> VO(MoO <sub>4</sub> )].6H <sub>2</sub> O	3430, 3227	2929	1544	1628	891	765
[(Dien-4H)(CHC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> VO(MoO <sub>4</sub> )].10H <sub>2</sub> O	3430	2928	1543	1629	897	761
[(Dien-4H)(CCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> VO(MoO <sub>4</sub> )].6H <sub>2</sub> O	3432	2924	1545	1620	898	777

 wave number in cm<sup>-1</sup>

 TABLE IV ANTIBACTERIAL STUDIES ON [(Trien-4H)(CHC<sub>6</sub>H<sub>4</sub>OH)<sub>2</sub>VO(MoS<sub>4</sub>)].10H<sub>2</sub>O DIAMETER OF THE INHIBITORY ZONE IN MM

SL No	microorganism	Inhibitory zone diameter in mm					
		1000µg	500 µg	250 µg	125 µg	dmsO	Streptomycin 10 µg
1	<i>S.aureus</i>	11	10	9	7	-	19
2	<i>Acinobacter</i>	12	13	8	7	-	10

Elemental analysis data on the complexes are shown in Table I which agrees with the proposed composition of the complexes. The complexes are highly soluble in DMSO, insoluble in alcohol and CHCl<sub>3</sub>. TG, DTG and DTA data on the complexes are shown in Table II. All the complexes have water of hydration indicated by endotherms below 100<sup>o</sup> C in the corresponding DTA curves. The complexes start losing water molecule above 60<sup>o</sup>C onwards, indicating less thermal stability. However loss of water is not a discrete step. Further decomposition of all the complexes lead to the formation of sulphide or oxide residues namely VOMoS<sub>4</sub> /VOMoO<sub>4</sub> which further get reduced to metallic state in the corresponding complexes. From 200<sup>o</sup> C to 500<sup>o</sup> C, a sharp decrease in weight shows the loss of schiff base ligands from the complexes. This stage is indicated by a number of exotherms and endotherms in the DTA. The molar conductance of the complexes in DMSO range around 5 ohms<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup> indicating non electrolytic nature. The molybdate complexes with salicylaldehyde based schiff bases, directly reduce to metal state while in molybdate complexes with acetophenone based Schiff bases, reduction to metal does not happen even by 1400<sup>o</sup> C. In tetrathio molybdate complexes both stages i.e conversion to VOMoS<sub>4</sub> and Metallic state could be seen. The plot of magnetic moment in emu vs magnetic field in gauss for the complexes do not run parallel to x axis indicating paramagnetic nature of

the complexes. From the slope, the magnetic moment obtained ranges from 1.76 B. M to 2.03 B.M. This indicates the presence of one unpaired electron per molecule. A higher value may indicate orbital contribution to the magnetic moment. It may therefore be inferred that Van in (+4) oxidation state ( $d^1$  system) and Molybdenum in (+6) oxidation state ( $d^0$  system) as seen with the precursors used for the synthesis of the complexes. The EPR spectra of the tetrathiomolybdate and oxomolybdate complexes with trien- salicylaldehyde are shown in figures 1 and 2 respectively. The room temperature EPR spectra show eight lines which are due to hyperfine splitting arising from the interaction of the unpaired electron with a  $^{51}\text{V}$  nucleus having the nuclear spin  $I = 7/2$ <sup>10</sup>. This confirms the presence of a single oxovanadium (IV) cation as the metallic centre in the complexes. The  $g$  values calculated for the two complexes are 2.17 and 2.03 respectively. The electronic spectra of the complexes show absorbance in the region 320 to 380 nm corresponding to  $d \rightarrow d$  transitions of vanadyl cation ( $d^1$ ). The absorbance below 280 nm corresponds to ligand transitions. The band around 480 nm in the tetrathio molybdate complexes may correspond to the sulphur to vanadium charge transfer. IR spectral assignment of the bands are given in Table III.  $\nu_{\text{NH}}$  and  $\nu_{\text{OH}}$  in the complexes appear around  $3400 \text{ cm}^{-1}$ .  $\nu_{\text{C=N}}$  appears in the region  $1625\text{-}1660 \text{ cm}^{-1}$  while  $\nu_{\text{C=C}}$  appears in the region  $1500\text{-}1600 \text{ cm}^{-1}$ .  $\nu_{\text{Mo=O}}$  and  $\nu_{\text{Mo-S}}$  of the complexes appear in the region  $930\text{-}970 \text{ cm}^{-1}$  and  $870\text{-}890 \text{ cm}^{-1}$  respectively.  $\nu_{\text{Mo-S}}$  appear in the region  $760\text{-}800 \text{ cm}^{-1}$ <sup>11-12</sup>.  $\nu_{\text{V=O}}$  appears in the region around  $500 \text{ cm}^{-1}$  in all complexes. Antibacterial studies were carried out on tetrathiomolybdate complex with trien-salicylaldehyde Schiff base against two organisms namely *S.aureus* and *Acinetobacter*. The species of bacteria were streaked on nutrient agar plates. Streptomycin was used as standard and DMSO as the negative control. The plates were then incubated at  $37^\circ\text{C}$  for 24 h. The inhibitory zones were then measured. The results of the antibacterial studies are given in Table-IV. The sample has given best results with the two bacteria especially with *Acinitobacter* at 1000 micro gram showing the diameter of inhibitory zone as 18 mm. Based on the above discussions, the complexes may tentatively be proposed a structure with two imine nitrogens of Schiff base ( $\text{CH=N}$ ) coordinated to vanadyl ie  $\text{VO}^{2+}$  group which is further linked to  $\text{MoX}_4^{2-}$  through two X where X= S or O.

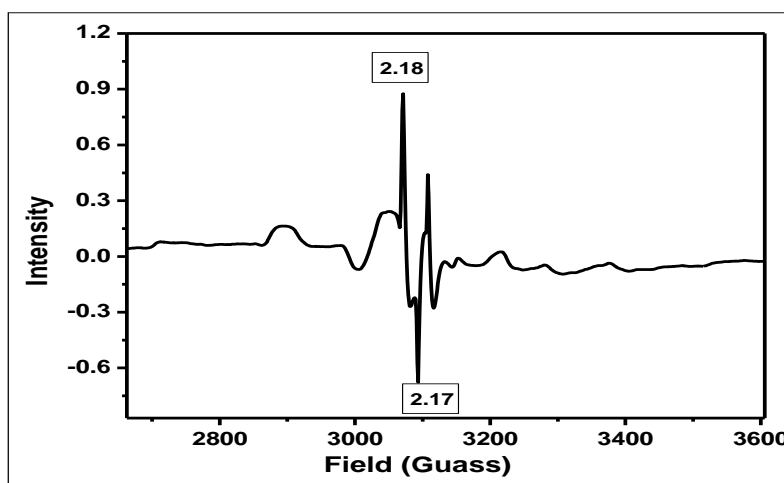


Fig-1 EPR spectrum of  $[(\text{Trien-4H})(\text{CHC}_6\text{H}_4\text{OH})_2\text{VO}(\text{MoS}_4)].10\text{H}_2\text{O}$

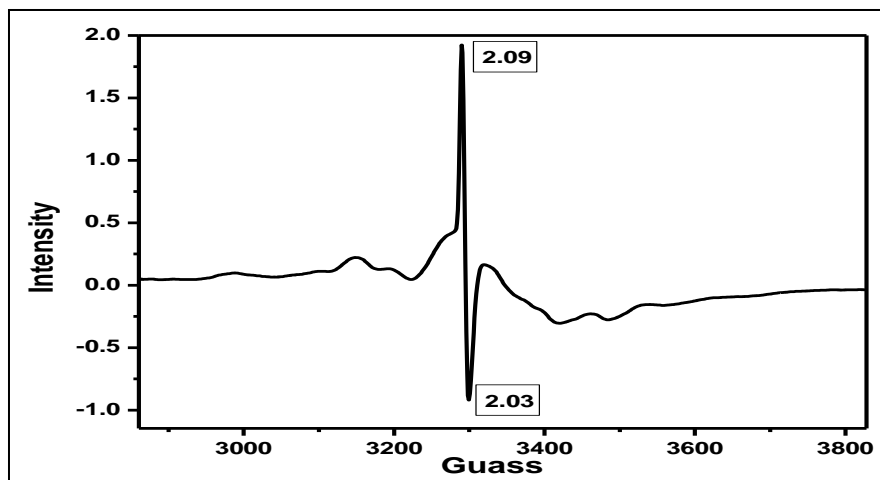


Fig- 2 EPR spectrum of  $[(\text{Trien-4H})(\text{CHC}_6\text{H}_4\text{OH})_2\text{VO}(\text{MoO}_4)].6\text{H}_2\text{O}$

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