



Synthesis and electrochemical characterisation of Molybdenum(VI) complexes of disalicylaldehyde malonoyl-dihydrazone



Aziz Ahmed^{a,*}, Ram A. Lal^b

^a Department of Chemistry, Indian Institute of Technology, Patna-13, Bihar, India

^b Department of Chemistry, North Eastern Hill University, Shillong 793 022, Meghalaya, India

HIGHLIGHTS

- Molybdenum(VI) complexes.
- The complexes were characterized by ¹H NMR, IR, UV–Vis and CV spectroscopy.
- The dihydrazone coordinates to Mo(VI) centre as neutral bidentate ligand.
- The ligand present in keto enol form in the complexes.

ARTICLE INFO

Article history:

Received 13 February 2013

Received in revised form 29 April 2013

Accepted 20 May 2013

Available online 1 June 2013

Keywords:

Molybdenum (VI) complexes
Disalicylaldehyde malonoyldihydrazone
Electrochemical behaviour

ABSTRACT

Molybdenum(VI) complexes composition $[(\mu_2-O)_2(MoO_2)_2(H_4L)_2] \cdot 2A$ (where $H_4L = H_4slmh$; $A = H_2O$ (1), pyridine (py, 2), 2-picoline (2-pic, 3), 3-picoline (3-pic, 4), 4-picoline (4-pic, 5)) have been isolated in solid state from the reaction of $MoO_2(acac)_2$ and disalicylaldehyde malonoyldihydrazone in 1:1 M ratio in ethanol at higher temperature. The complexes have been synthesised and characterised by various physico-chemical and spectroscopic studies. The structure of the molybdenum(VI) of all complexes has been established by elemental analyses, electronic, IR, ¹H NMR and CV spectral studies. The dihydrazone is coordinated to the metal centres in keto enol form in all the complexes (1)–(5). The electronic spectra of the complexes are dominated by strong charge transfer bands. All of the complexes involve six coordinated molybdenum centre with octahedral arrangement of donor atoms.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Molybdenum has been found to be an important element in biological systems. The significant enzymatic role of molybdenum in biochemical reactions [1–3] specially in the oxidation of aldehydes, purines and sulphides [4] induced the chemists to use the molybdenum complexes as biomimetic catalysts in the oxygenation of organic compounds [5,6]. In this light, molybdenum(VI) dioxo-complexes have been extremely investigated [7–9] particularly with respect to the catalytic role of transferase enzymes like nitrate reductase in which their active sites consist of a *cis*-molybdenum dioxo moiety [10,11]. The ability of molybdenum to formation of stable complexes with oxygen-, nitrogen- and sulphur-containing ligands led to development of molybdenum Schiff base complexes which are efficient catalysts both in homogeneous and heterogeneous reactions [12–15]. The activity of these complexes varied markedly with the type of ligands

and coordination sites [16]. The useful role of molybdenum is not restricted to biological systems only, but it also plays important roles in a variety of chemical reactions such as hydrodesulphurisation, oxygen transfer reactions (e.g., olefin Epoxidation [17]) and olefin metathesis [18]. The *cis*-dioxo molybdenum compounds display catalytic activities [19], are models for enzymes [20,21] and are very useful material precursors [22]. Catalytic activity is frequently linked to coordinative unsaturation and the active site in various molybdenum oxidation catalyst are believed to contain coordinately unsaturated molybdenum centres [23–25].

A survey of literature suggests that complexes of dihydrazones derived from first series transition metal ions have been described in some details, those of molybdenum have received scant attention only. Acyl-, aroyl- and pyridoyldihydrazones containing amide, azomethine, and phenol are polyfunctional ligands which react with metal ions either in the keto or the enol form [26]. Although a few complexes of metal ions with dihydrazones derived from condensation of salicylaldehyde and acyl-, aroyl- and pyridoyldihydrazones have been reported, work done on dihydrazones

* Corresponding author.

E-mail address: azizahmed@iitp.ac.in (A. Ahmed).

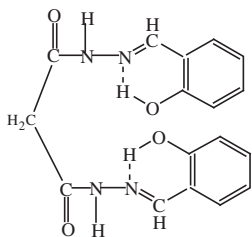


Fig. 1a. Skeleton of the ligand *N,N'*-bis(2-hydroxyphenyl) propanedionyl dihydrazone (H_4slmh).

containing active methylene functions and bulky phenol fragments in their molecular skeleton is virtually absent [27–31]. In view of the significant role played by molybdenum in biological systems and as a catalyst in chemical reactions and virtual absence of work on molybdenum complexes derived from the title ligand disalicylaldehyde malonoyldihydrazone (Fig. 1a) have been investigated. The resulting products from such reactions have been characterised by various techniques and spectroscopic studies and are reported in the present article.

2. Experimental

Ammonium molybdate ($(NH_4)_6MoO_6 \cdot 4H_2O$), diethylmalonate $CH_2(CO_2Et)_2$, hydrazine hydrate ($N_2H_4 \cdot H_2O$), salicylaldehyde ($C_6H_4(OH)CHO$) were E-Merck or equivalent grade reagents. The ligand disalicylaldehyde malonoyldihydrazone was prepared in two steps. In the 1st step, malonoyl- (H_6mh) was prepared by reacting diethylmalonate with hydrazine hydrate in 1:2 M ratio. In the second step, malonoyl-dihydrazine thus obtained were allowed to react with salicylaldehyde in 1:2.2 M ratio in ethanol which yielded the ligand $H_4slmh(H_4L)$, $MoO_2(acac)_2$ was prepared by a reported method [32].

The reactions were carried out in open air and the ethanol used as solvent is 95%. The estimation of molybdenum was done by following the standard literature procedure [33]. Room temperature magnetic susceptibility measurements were carried out on Sherwood Scientific Magnetic susceptibility Balance MBS-Auto. The molar conductance of the complexes at 10^{-3} M dilution in DMSO solution were measured on Wayne Kerr Precision Component Analyser 6440B with a dip-type conductivity cell at room temperature. Infrared spectra were recorded on Bomem A-8FT-IR Spectrophotometer in the range $4000\text{--}450\text{ cm}^{-1}$ in KBr discs. The electronic spectra were recorded on a Perkin Elmer Lambda 25 UV/Vis spectrophotometer using DMSO solution.

Table 1
Complexes, colour, decomposition point, elemental analysis, molar conductance, electronic spectral bands (λ_{max} (nm) for molybdenum(VI)) complexes of disalicylaldehyde malonoyldihydrazone.

Sl no.	Complex and colour	D.P (°C)	Yield (%)	Elemental analysis: found (cal)%				Molar conductance ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$)	Electronic spectral bands λ_{max} (nm), ϵ_{max} ($\text{dm}^3\text{ cm}^{-1}\text{ mol}^{-1}$)
				Mo	C	H	N		
L	H_4slmh White	223	75	–	60.37(60.00)	4.71(4.74)	16.28(16.46)	–	280(333367), 323(10267)
1	$[(\mu_2-O)_2(MoO_2)_2(H_4slmh)_2] \cdot 2H_2O$ Yellow	>300	70	19.19(19.10)	40.84(40.64)	3.65(3.61)	10.74(11.14)	0.5	290(27200), 324(20500), 404(3500)
2	$[(\mu_2-O)_2(MoO_2)_2(H_4slmh)_2] \cdot 2py$ Yellow	>300	69	17.21(17.03)	46.56(46.90)	3.73(3.76)	12.29(12.43)	1.7	295(26400), 321(22600), 403(3100)
3	$[(\mu_2-O)_2(MoO_2)_2(H_4slmh)_2] \cdot 2(2-pic)_2$ Green	>300	72	16.75(16.62)	48.02(47.84)	4.00(4.02)	11.98(12.12)	3.2	294(31100), 320(26900), 405(2900)
4	$[(\mu_2-O)_2(MoO_2)_2(H_4slmh)_2] \cdot 2(3-pic)$ Green	>300	65	16.89(16.62)	47.37(47.84)	4.06(4.02)	12.38(12.12)	1.0	293(30700), 318(29604), 403(3050)
5	$[(\mu_2-O)_2(MoO_2)_2(H_4slmh)_2] \cdot 2(4-pic)$ Light Green	>300	68	16.96(16.62)	47.54(47.84)	4.05(4.02)	12.53(12.12)	0.8	293(29840), 324(20388), 404(2980)

The 1H NMR spectra were recorded on Varian EM 390 MHz in DMSO- d_6 using TMS as internal standard. The Cyclic Voltammetric measurement of the complexes in DMSO (10^{-3} M) was done using CH Instruments Electrochemical Analyser under nitrogen atmosphere. The electrolytic cell comprises of 3-electrodes. The working electrode was a glassy carbon disk from BAS and the reference electrode was a aqueous SCE or Ag/AgCl separated from the sample solution by a salt bridge, 0.1 M TBAP was used as the supporting electrolyte.

3. Preparation of $[(\mu_2-O)_2(MoO_2)_2(H_4L)_2] \cdot 2A$ (where $H_4L = H_4slmh$, $A = H_2O$ (1), pyridine (2), 2-picoline (3), 3-picoline (4) and 4-picoline (5))

In order to prepare the complex $[(\mu_2-O)_2(MoO_2)_2(H_4L)_2] \cdot 2A$ (1), bis(acetylacetonato) dioxomolybdenum(VI) (1.06 g, 3.25 mmol) in hot ethanol (25 mL) was mixed with H_4slmh (1.00 g, 2.94 mmol) in hot ethanol (30 mL). The resulting reaction mixture was stirred for about 15 min at 70°C followed by refluxing for $1\frac{1}{2}$ h. The orange coloured precipitate so obtained was filtered in hot condition and washed with ethanol, ether and dried over $CaCl_2$. Yield: 1.46 g.

The complexes (2)–(5) were also prepared essentially by the above procedure by adding pyridine and pyridine bases to the solution obtained by mixing $MoO_2(acac)_2$ and dihydrazone in 1.1:1 M ratio and refluxing the reaction mixture for $1\frac{1}{2}$ h. This precipitated yellow coloured precipitate, which was filtered in hot condition, washed with ethanol, ether and dried over anhydrous calcium chloride.

4. Results and discussion

The characterisation data of the complexes have been given Table 1. On the basis of various analytical data, the complexes have been suggested to have stoichiometry $[(\mu_2-O)_2(MoO_2)_2(H_4L)_2] \cdot 2A$ (where $H_4L = H_4slmh$: $A = H_2O$ (1), py (2), 2-pic (3), 3-pic (4) and 4-pic (5)). All of the complexes are yellow, green and light green respectively. They are air stable and melt with decomposition above 300°C . All the complexes are completely soluble in coordinating solvents like DMSO and DMF. They are insoluble in water and other common organic solvents such as ethanol, methanol, acetone, $CHCl_3$, CCl_4 , ether and benzene. All of the complexes are diamagnetic indicating the presence of molybdenum in +6 oxidation state.

A consistent effort to crystallize the complexes either from saturated solution or by diffusing into saturated solution in CH_3CN , DMSO and DMF in a closed system led to the precipitation

Table 2
Structurally significant ^1H NMR spectral data (in ppm) for molybdenum(VI) complexes derived from disalicylaldehyde malonyldihydrazone.

Sl. no.	Ligand/Complex	$\delta\text{-CH}_2$	$\delta\text{-phenyl}$	$\delta\text{-CH=N}$	$\delta\text{-(NH)}$	$\delta\text{-(OH)}$	$\delta\text{-C}_2\text{H}_5\text{OH}$	$\delta(\text{py}/\alpha/\beta/\gamma)$
L	H_4slmh	3.61(s) 3.91(s)	6.65–7.77(m)	8.42(s) 8.28(s)	10.03(s)	11.60(d, 82.5 Hz) 11.25(d, 82.5 Hz)	–	–
1	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2]\cdot 2\text{H}_2\text{O}$	3.61(s) 3.91(s)	6.65–7.71(m)	8.79(s) 8.41(s)	11.05 (d, 10 Hz)	11.75(d, 112.5 Hz) 12.17(d, 112.5 Hz) 11.43($\delta\text{-OH}$ enol)	–	–
2	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2]\cdot 2(\text{py})$	3.62(s) 3.92(s)	6.70–7.70(m)	8.68(d, 53 Hz) 8.34(d, 53 Hz)	11.07(s) 10.03(s)	11.90(d, 12 Hz) 11.49(d, 12 Hz) 11.43($\delta\text{-OH}$ enol)	–	8.56(8.61) ^a
3	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2]\cdot 2(2\text{-pic})$	3.61(s) 3.92(s)	6.89–7.70(m)	8.78(s) 8.40(s)	11.06(s) 11.03(s)	11.90(d, 30 Hz) 11.48(d, 30 Hz) 11.42($\delta\text{-OH}$ enol)	–	8.44(8.48) ^a 2.50(2.55) ^b
4	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2]\cdot 2(3\text{-pic})$	3.78(s) 3.99(s)	6.75–7.73(m)	8.81(s) 8.80(s)	11.05(s) 10.02(s)	11.90(d, 42 Hz) 11.44(d, 42 Hz) 11.45($\delta\text{-OH}$ enol)	–	8.42(8.43) ^a 2.31(2.32) ^b
5	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2]\cdot 2(4\text{-pic})$	3.77(s) 3.92(s)	6.65–7.80(m)	8.42(s) 8.28(s)	11.04(s) 11.0(s)	11.90(d, 22.5 Hz) 11.46(d, 22.5 Hz) 11.48($\delta\text{-OH}$ enol)	–	8.79(8.60) ^a 2.35(2.37) ^b

^a *o*-proton signal of py/2-pic/3-pic/4-pic.

^b Methyl proton signal of 2-pic/3-pic/4-pic.

of amorphous products. Such behaviour of the complexes with regard to their crystallization prevented their analyses by X-ray crystallography.

The complex (1) shows weight loss at 110 °C indicating the possibility of presence of water molecules in their lattice structure. On the other hand, the remaining complexes do not show any weight loss at this temperature ruling out the possibilities of presence of coordinated water molecules to the metal centre. However, the complexes (2)–(5) showed weight loss at 180 °C corresponding to two py/2-pic/3-pic/4-pic molecule [34]. The expulsion of these donor molecules at this temperature indicates that they are uncoordinated to the metal centres.

4.1. Molar conductance

All of the complexes have molar conductance value in the region 0.5–3.2 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ in DMSO solution at 10^{-3} M dilution. These values are consistent with the non-electrolytic nature of the complexes in this solvent [35].

4.2. Electronic spectra

The important electronic spectral bands for dihydrazone ligand and molybdenum complexes along with molar extinction coefficients have been given in Table 1. The electronic spectra of the complexes were recorded between 270 and 800 nm in DMSO as the solvent. The free ligand shows band at 280 and 323 nm are assigned to arise due to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition due to $>\text{C}=\text{N}$ and $>\text{C}=\text{O}$ groups in the ligand [36]. The band at ~ 323 nm is considered as characteristic band for salicylaldehyde fraction of the ligand as has been observed in monoacylhydrazones [37]. Since H_4slmh is not expected to be chromophoric in the visible region and the complexes (1)–(5) are diamagnetic, these bands have been assigned as the ligand–metal charge transfer (LMCT) transition on the basis of their high molar extinction coefficients. They may, most probably, be associated with a ligand–metal charge transfer originating from an electronic excitation from HOMO of phenolic oxygen to LUMO of molybdenum [38].

4.3. Proton nuclear magnetic resonance spectroscopy

The ^1H NMR spectra of the ligand and the molybdenum(VI) complexes have been set out in Table 2. The ^1H NMR of the

ligand and the complexes (4), (5) are shown in Figs. 5a, 5b, 2a, 2b, 3a, and 3b. The ^1H NMR spectrum of H_4slmh show two doublets in the region δ 11.25 and 11.60 along with a singlet at 10.03 ppm downfield of TMS. These signals are assigned to $-\text{OH}$ protons and secondary-NH protons. Further, two signals are observed at δ 8.28 and 8.42 ppm in ^1H NMR spectra of dihydrazone which owe their origin due to azomethine proton. A multiplet observed in the region δ 6.65–7.77 ppm is assigned to aromatic protons. The methylene protons appear as two singlets at δ 3.61 and 3.91 ppm in the dihydrazone, indicating keto-enol equilibrium in solution [39]. The signal at 3.61 ppm is attributed to methylene protons ($-\text{CH}_2-$) that at 3.91 ppm is attributed to methine proton ($=\text{CH}-$). The appearance of two signals in H_4slmh and their positions are consistent with the enolization of dihydrazone involving active methylene protons. Thus, the enolization processes in H_4slmh involving active methylene and secondary $-\text{NH}$ protons are shown in Fig. 1b.

As it is evident from the structural formula of the dihydrazone Fig. 1a, there are only four types of phenyl protons, interestingly, H_4slmh shows seven signals in the region δ 6.65–7.77 ppm such features associated with aromatic protons suggest that the two phenyl rings in H_4slmh are in different planes. It is imperative to mention that one phenyl ring in H_4slmh is in equatorial plane. The two proton signals observed for dihydrazone observed at δ 11.25 and 11.60 ppm assigned to δ OH protons appear in all of the complexes and possess essentially the same features as those observed in the free ligand. However, these signals are downfield shifted by 0.15–0.30 ppm in the complexes. Such a shifting of these signals might arise either due to co-ordination of protonated phenolic-OH groups or involvement of these phenolic-OH groups in a new kind of hydrogen bonding. The azomethine proton signals are downfield shifted in all of the complexes by δ 0.06–0.37 ppm. Such a downfield shift of azomethine proton signal is caused by drainage of electron density from azomethine nitrogen atoms to the metal centre [40,41]. In all the complexes the signals $\delta\text{-CH=N}$ appear as either two doublets or two singlet.

All of the complexes show an easily identifiable additional resonance in the region δ 8.42–8.56 ppm. These signals are attributed to arise due to ortho-protons of pyridyl ring of pyridine, 2-picoline, 3-picoline and 4-picoline molecules. The *o*-protons of pyridyl ring of free pyridine bases absorb at δ 8.61, 8.48, 8.43 and 8.60 ppm, respectively. Further, a new signal appears in

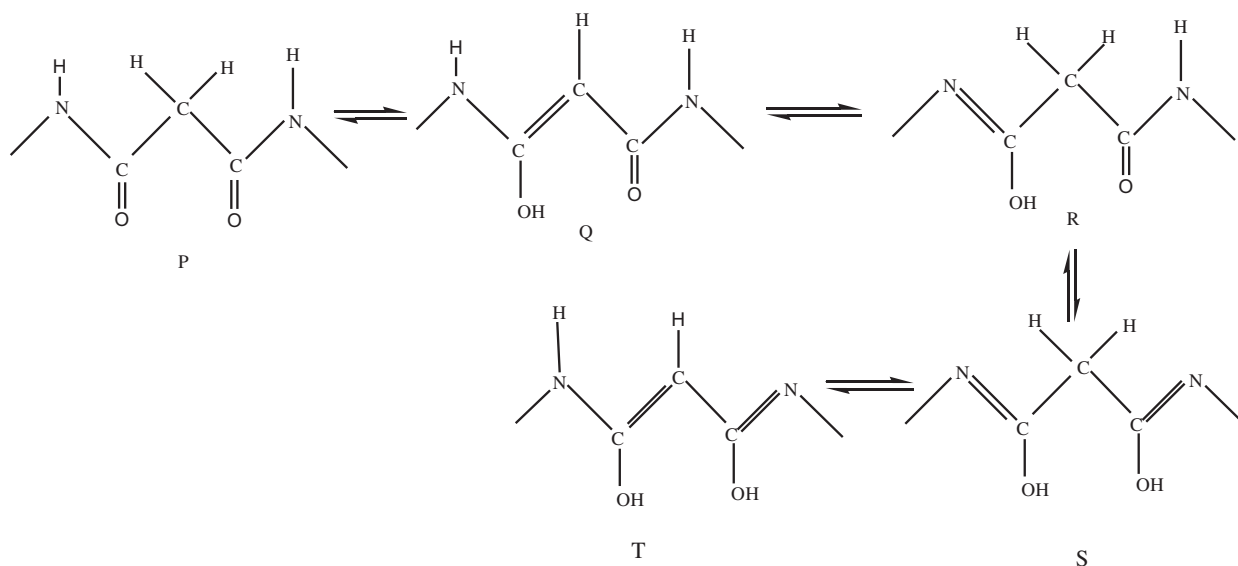


Fig. 1b. Showing the enolization process in the ligand H4slmh involving active methylene and secondary –NH proton.

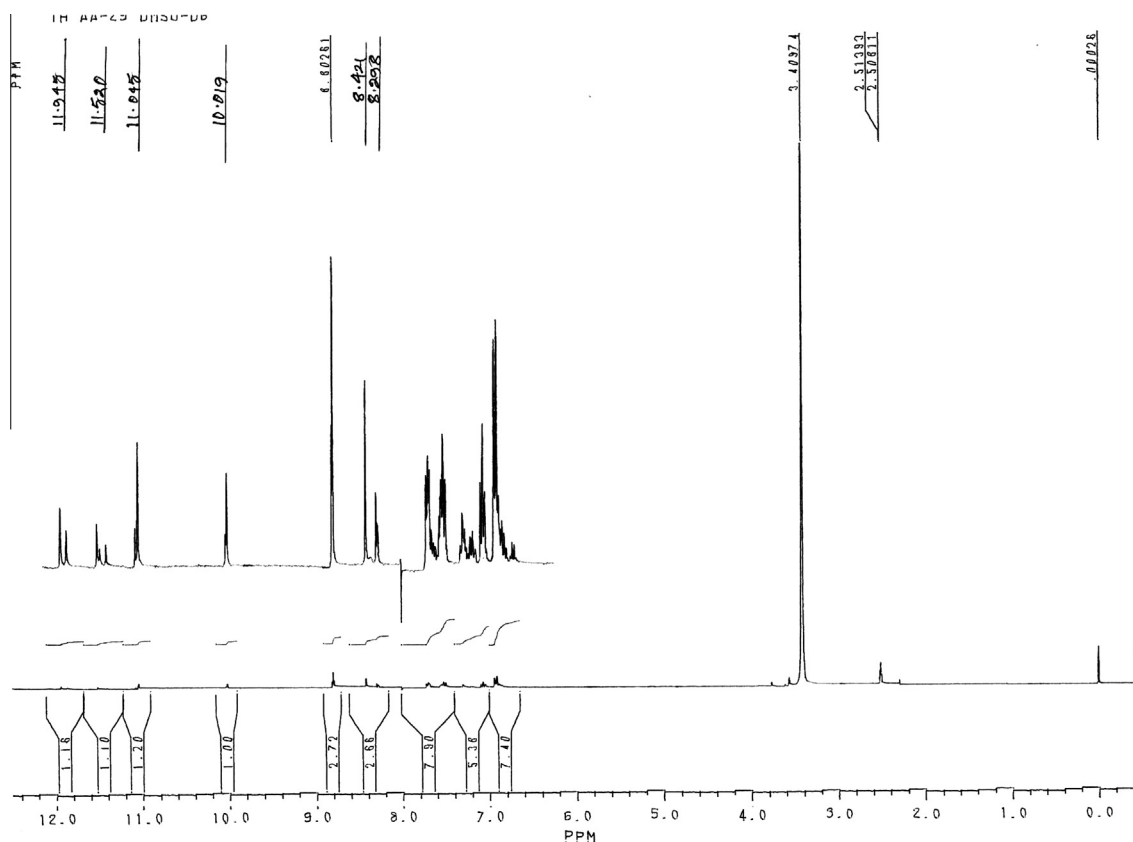


Fig. 2a. ^1H NMR Spectrum of $[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2]\cdot 2(3\text{-pic})$ (**4**) in DMSO-d_6 .

the region δ 2.31–2.50 ppm in all of the complexes which is assigned to methyl proton. The methyl proton signals appear at δ 2.55, 2.32 and 2.37 ppm in free 2-picoline, 3-picoline and 4-picoline molecules, respectively. A comparison of the position of *o*-pyridyl protons and methyl protons in pyridine and substituted pyridines in the complexes with their positions in the free pyridines suggests that they are all upfield shifted in the complexes.

This upfield shift of pyridyl and methyl protons has been related to non-coordination of pyridine and substituted pyridines to the Mo centre.

Further, no additional signal is observed in the downfield region in the ^1H NMR spectra of the complexes (1–5) which may be assigned to 2-pyridyl proton of pyridine, 3-picoline and 4-picoline molecules, respectively [42]. Rather upfield shift of the pyr-

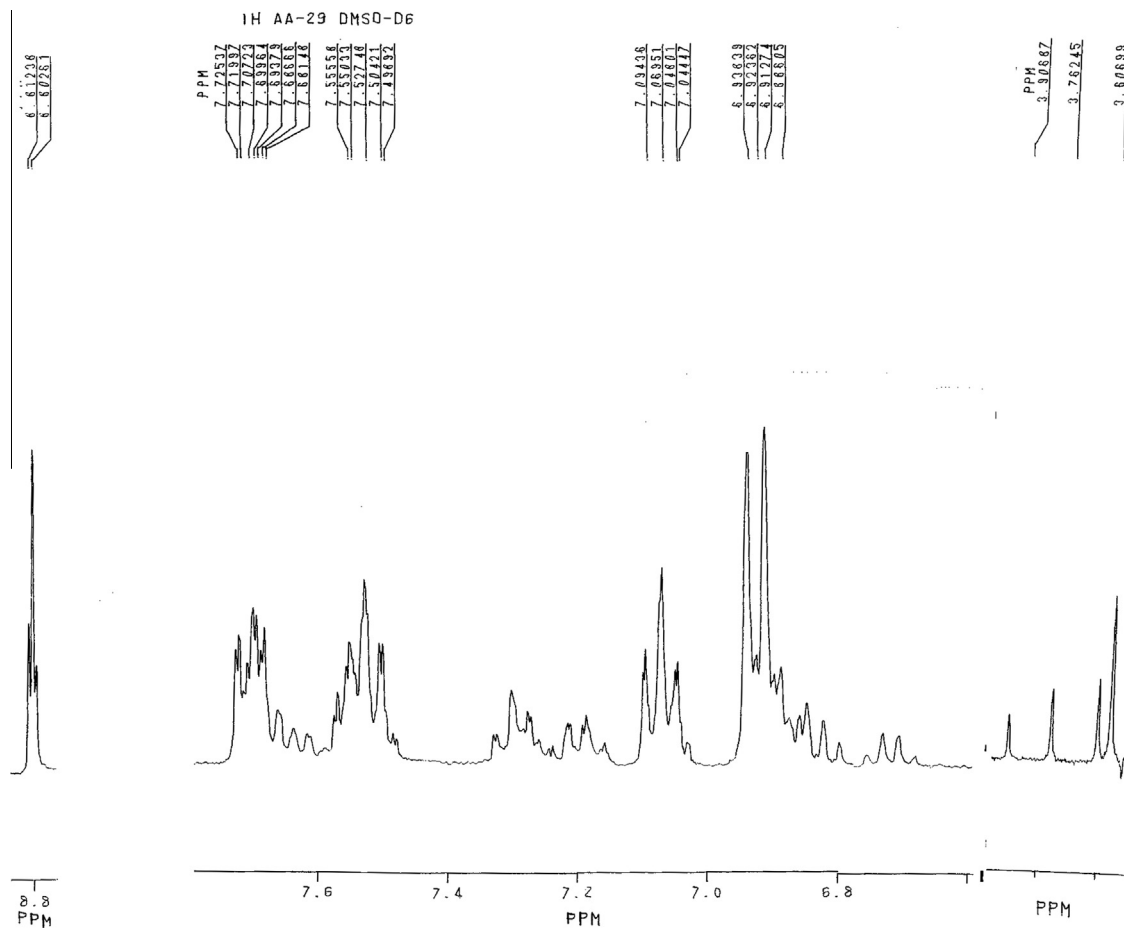


Fig. 2b. ¹H NMR Spectrum of [(μ₂-O)₂(MoO₂)₂(H₄slmh)₂] \cdot 2(3-pic) (4) in DMSO-d₆(Extended scale).

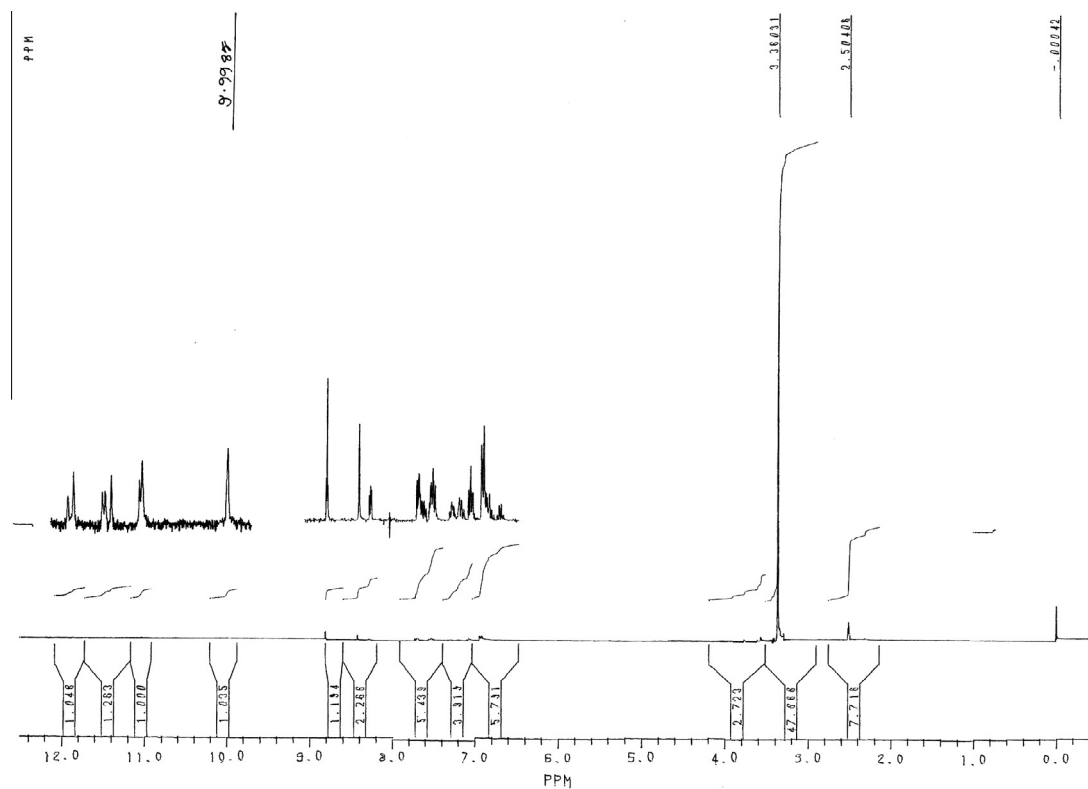


Fig. 3a. ¹H NMR Spectrum of [(μ₂-O)₂(MoO₂)₂(H₄slmh)₂] \cdot 2(4-pic) (5) in DMSO-d₆.

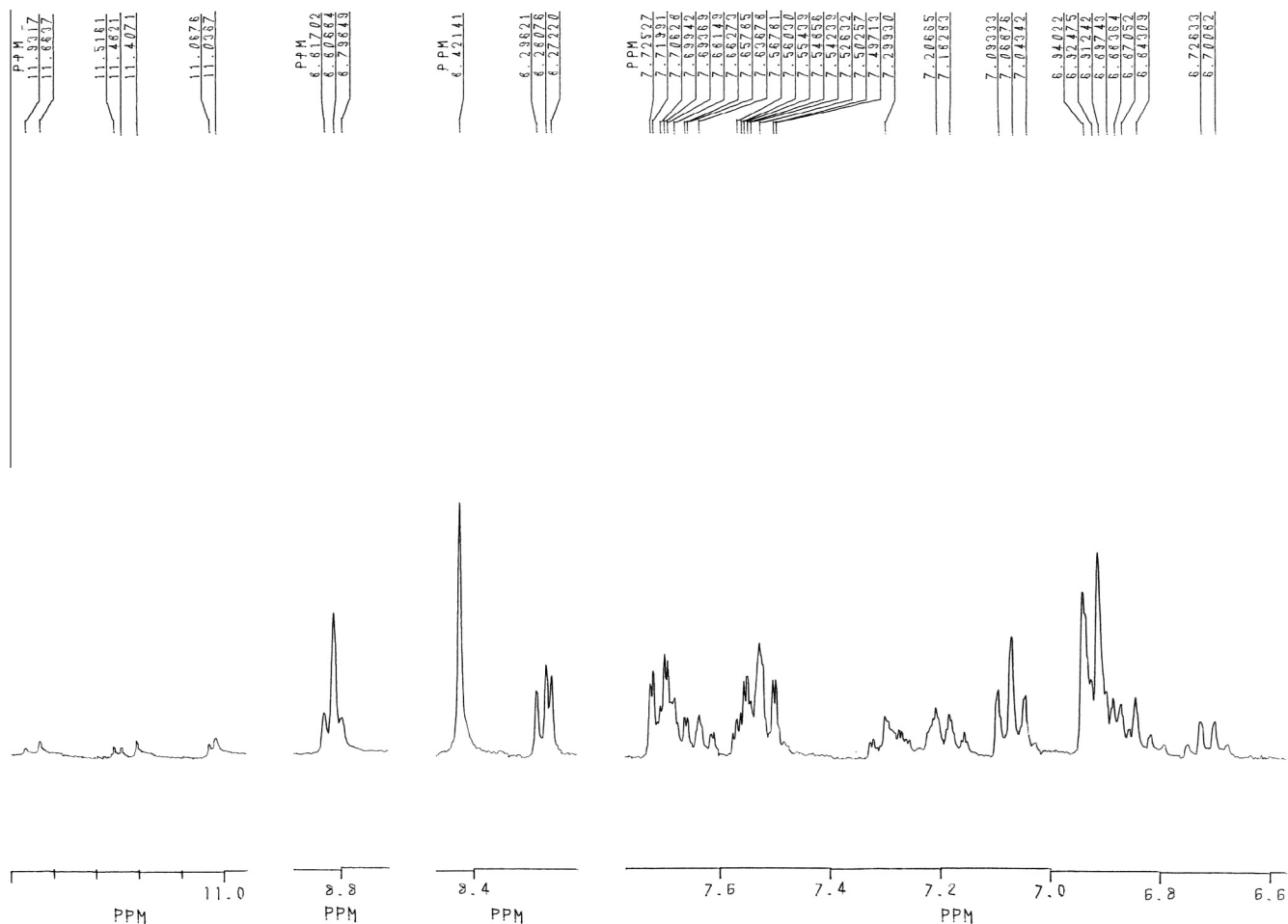


Fig. 3b. ^1H NMR Spectrum of $[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2]\cdot 2(4\text{-pic})$ (**5**) in DMSO-d_6 (Amplified Form).

Table 3

Structurally significant IR spectral data (in cm^{-1}) for molybdenum(VI) complexes derived from disalicylaldehyde malonyldihydrazone.

Sl. no.	Ligand/complex	$\nu\text{OH} + \text{NH}$	$\nu\text{C}=\text{O}$	$\nu\text{C}=\text{N}$	Amide II + $\nu\text{C}-\text{O}$ Phenolic	$\nu\text{C}-\text{O}$	$\nu\text{N}-\text{N}$	$\nu\text{M}=\text{O}$	$\nu\text{M}-\text{O}$ Phenolic	$\nu\text{M}-\text{O}$ Carbonyl
L	H_4slmh	3436m 3277m 3071m	1679vs	1619m	1566m	1268s	1036w	-	-	-
1	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2]\cdot 2\text{H}_2\text{O}$	3600- 3000 3277sbr 3065s	1679s	1613s	1553s	1268s	-	917s	585s	466w
2	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2]\cdot 2(\text{py})$	3423m 3283m 3071m	1679vs	1613vs	1553s	1268s	1043w	910vs 758s	572m	459w
3	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2]\cdot 2(2\text{-pic})$	3562ssh 3277m 3071m	1686s	1613vs	1560s	1268s	1036w	956m 917s 771s	579m	466w
4	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2]\cdot 2(3\text{-pic})$	3660msh 3283m 3184m 3065m	1679vs	1613vs	1560s	1268s	1036w	956m 917vs 771s	579m	459w
5	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2]\cdot 2(4\text{-pic})$	3283m 3065m	1679vs	1619vs	1560s	1268s	1043w	956m 923s 771s	579m	466w

idyl and methyl protons of pyridine, 2-picoline, 3-picoline and 4-picoline molecules is observed. This suggests the possibility of presence of pyridine/2-picoline/3-picoline/4-picoline molecule

in the lattice of the complexes and further rules out the possibility of coordination of ring nitrogen atoms of these donor molecules to the metal centre.

Table 4

The electrochemical parameters for the Molybdenum(VI) complexes of disalicylaldehyde malonoyldihydrazone.

Sl. no	Complex	Epa/V	Epc/V	ΔE_p
1	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2] \cdot 2\text{H}_2\text{O}$	+0.06	-1.02	+1.08
2	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2] \cdot 2(\text{py})$	+0.44	-0.56	+1.00
3	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2] \cdot 2(2\text{-pic})$	-1.11	-1.56	+0.45
		-0.40	-1.00	+0.6
		+0.26	-0.23	+0.49
4	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2] \cdot 2(3\text{-pic})$	+0.59	-1.25	+1.84
5	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2] \cdot 2(4\text{-pic})$	-0.07	-0.43	+0.36
		+1.08	+0.66	+0.42

4.4. Infrared spectra

Structurally significant IR bands for the free ligand and their molybdenum(VI) complexes have been set out in Table 3. The IR spectra of the complexes (1) to (5) show a strong band in the region 3000–3600 cm^{-1} with a distinct band in the region 3184–3277 cm^{-1} are assigned to stretching vibrations of phenolic -OH and secondary -NH groups. The complex (1) shows weight loss at 110 °C indicating presence of two water molecules in the lattice structure of the complex. None of the complexes shows loss of weight at 180 °C which suggests the absence of water molecules in the coordination sphere of the complexes. However, the complexes (2)–(5) show loss of weight corresponding to two py/2-pic/3-pic/4-pic molecules at 190 °C. The loss of these donor molecules at such a high temperature indicates that they are present in the lattice structure of the complexes.

It is evident from Table 3 that the amide I band at 1679 cm^{-1} in free dihydrazone is almost unshifted except in (3) ruling out the possibility of coordination of ligand to the metal centre through carbonyl oxygen atoms. Similar results have been established in the dihydrazone metal complexes by Pelizzi and co-workers [43] from X-ray crystallographic study and spectroscopic study as well. The ligand shows single strong band 1619 cm^{-1} due to stretching vibration of $>\text{C}=\text{N}$ group. This band remains almost unshifted in position in the complex (5) while shifts to lower frequency by 6 cm^{-1} in the remaining complexes. Such a behaviour of $\nu\text{C}=\text{N}$ band in the complexes as compared to its position in the uncoordinated dihydrazone may be related to coordination of $>\text{C}=\text{N}$ group

to the metal centre. The unshifted position of $\nu\text{C}=\text{N}$ band in the complex (5) is due to difference of bonded species $>\text{C}=\text{N} \cdots \text{H}$ to $>\text{C}=\text{N} \rightarrow \text{M}$ and indicates that the strength of $>\text{C}=\text{N} \rightarrow \text{M}$ band in the complex is almost same as that of hydrogen bonding between $>\text{C}=\text{N}$ and OH group in the uncoordinated dihydrazone. The ligand band appearing at 1268 cm^{-1} may be assigned to stretching vibration of phenolic (C–O) groups. This band remains unshifted in position in the complexes (1)–(5). From such a feature associated with the phenolic (C–O) groups, we have refrained from drawing any conclusion regarding involvement of phenolic oxygen into bonding or otherwise. However, the possibility of involvement of new type of H-bonding involving phenolic–OH group cannot be ruled out.

The aromatic ring shows a weak absorption at 1600 cm^{-1} , in the present ligand, this band does not show its independent existence and appears to merged with $>\text{C}=\text{N}$ group vibration in the region 1619 (vs) cm^{-1} . Moreover, in the complexes also it does not show its independent existence, most probably, because of its overlapping with either $>\text{C}=\text{N}$ band or amide II band and $\nu(\text{C}=\text{O})$ phenolic band. The region below 1200 cm^{-1} is not well defined for hydrazide derivatives and contains bands due to N–N, C–N, C–H bending modes. Eliminating the bands due to C–H in-plane deformation in the region 1050–900 cm^{-1} in the ligand, a weak band at 1036 cm^{-1} has been assigned to $\nu\text{N}=\text{N}$ vibration. This band either shifts to higher frequency or remains almost unaltered in the complexes indicating involvement of only nitrogen atom of N–N group in coordination. All of the complexes exhibit two medium to strong bands in the region 956–910 cm^{-1} . The presence of two medium to strong bands in this region indicates the presence of *cis*- MoO_2^{2+} grouping in these complexes. The complexes (1–5) show a new strong band in the region 758–771 cm^{-1} . It is imperative to mention that uncoordinated ligand H_4slmh also possesses a medium intensity band at ~ 758 cm^{-1} , yet the intensity of the band in the region 758–771 cm^{-1} in the complexes (1)–(5) is more than that the band in corresponding free ligand. Hence, this band is assigned as arising from the asymmetric stretching (Mo_2O) of a bent

$\text{Mo}-\text{O}-\text{Mo}$ bridging [44]. The appearance of this band as low as in the region 758–771 cm^{-1} suggests that the bridging $\text{Mo}=\text{O} \cdots \text{Mo}$ band in these complexes is quite strong. From the above discussion, it is evident that the ligand co-ordinates to the

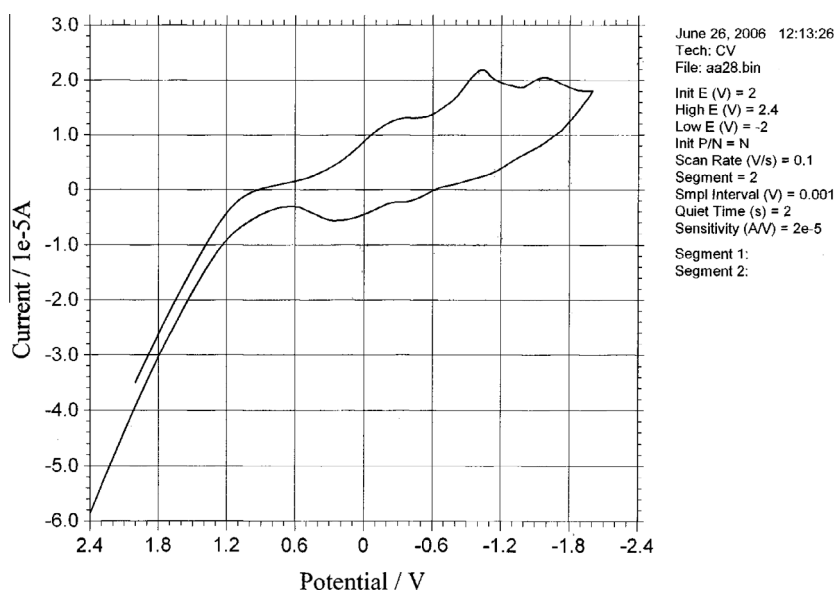


Fig. 4. Cyclic voltammogram of $[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2] \cdot 2(2\text{-pic})$ (3) in MSO.

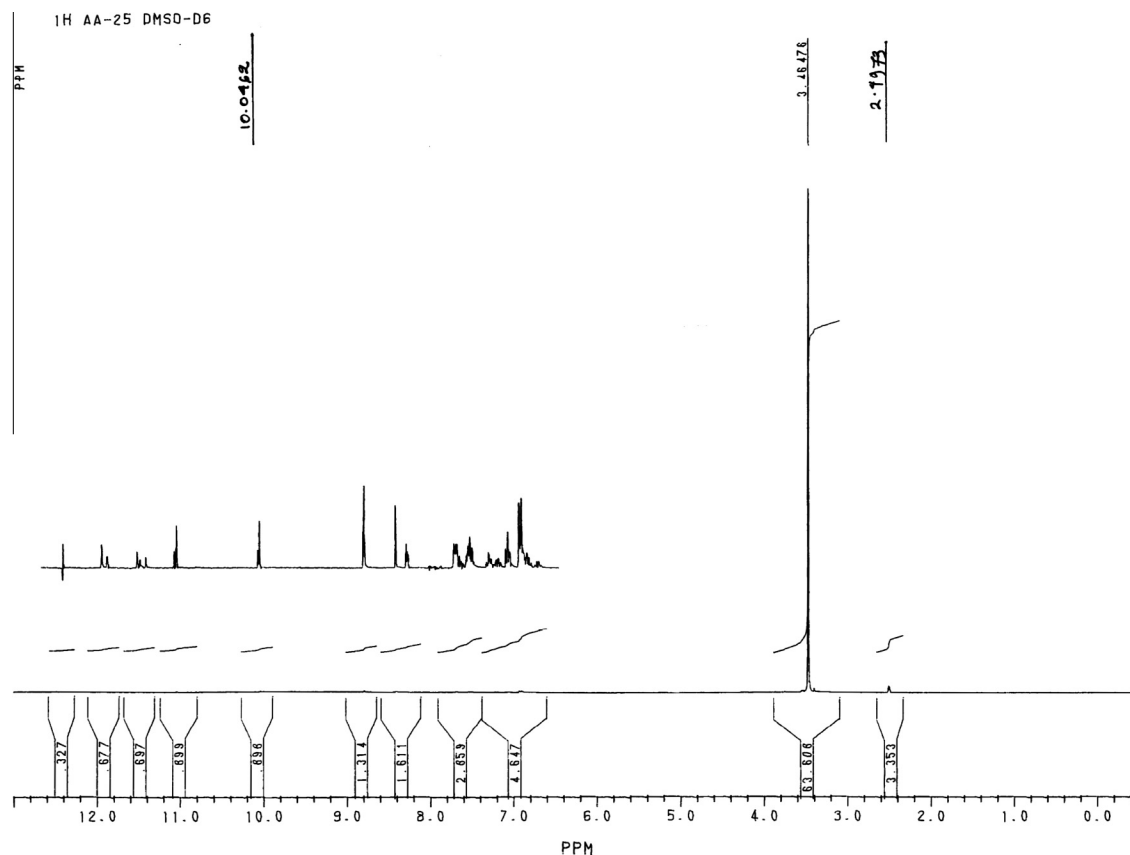


Fig. 5a. ^1H NMR Spectrum of the ligand in DMSO-d_6 (Integrated form).

metal ions in keto form as neutral bidentate ligand through azomethine nitrogen atoms only.

4.5. Low frequency IR

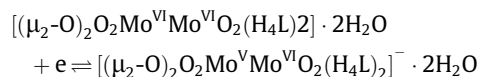
The low frequency IR of the complexes $[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2] \cdot 2\text{A}$ ($\text{A} = \text{H}_2\text{O}$ (1), py (2)), have been studied as representative examples in order to locate bands due to pyridine bases are shown below.

Sl. no	Complexes	$\nu(\text{M-N})$ (hydrazine)	Pyridine vibration
1	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2] \cdot 2\text{H}_2\text{O}$	341m 314m	405m
2	$[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{slmh})_2] \cdot 2\text{py}$	343m	397msh

The free pyridine bases show absorption bands at around 600 and $\sim 405\text{ cm}^{-1}$ [45] due to in-plane and out-of-plane ring deformation modes, respectively. The band 405 cm^{-1} shifts to higher frequencies upon complexation. In the present study, the complexes show a new medium to weak intensity band in the region $397\text{--}405\text{ cm}^{-1}$. This band either appears almost at the same position as in free pyridine or at lower position. This shows that the pyridine is not coordinated to the metal centre rather present in the lattice of the complexes. Moreover, these complexes do not show any band in the region $200\text{--}300\text{ cm}^{-1}$ in which may be assigned to stretching vibration of $\nu(\text{M-N})$ vibration of coordinated pyridine ruling out the possibility of coordination of pyridine molecules to the metal centres.

4.6. Cyclic voltammetry

The cyclic voltammograms of a 2 mM solution of the complexes have been recorded at a scan rate of 100 mV/s by cyclic voltammetry in DMSO solution due to their insolubility in non-coordinating organic solvents (CH_3CN and CH_2Cl_2) with a 0.1 M tetra-n-butyl ammonium perchlorate (TBAP) as a supporting electrolyte. The complexes (1) shows a reductive wave at -1.02 V and the corresponding oxidative wave is at $+0.06\text{ V}$ with ΔE_p of $+1.08\text{ V}$ (shown in Table 4). The ligand in the present study does not exhibit any redox activity in the potential range -2.4 to $+2.4$. Hence, these reductive and oxidative waves are attributed to arise due to electron transfer reactions centered on metal. Electrochemical studies on several *cis*-dioxomolybdenum(VI) complexes derived from multidentate nitrogen and oxygen donor ligands have generally shown irreversible or quasi-reversible behaviour. The high peak separation, most probably, results from a slow heterogeneous electron exchange rate rather than from intervening heterogeneous reactions. Accordingly, these reductive and oxidative waves are assigned to the following redox reaction.



The large separation between redox couples in complexes derived from bridging ligands have been reported by McCleverty et al. [46] in which it has been shown that the planarity and the relative short metal–metal separation result in greater redox separation ($\Delta E_{1/2}$). On the other hand, the 2-picoline complexes (3) shows three reductive and correspondingly three oxidative waves

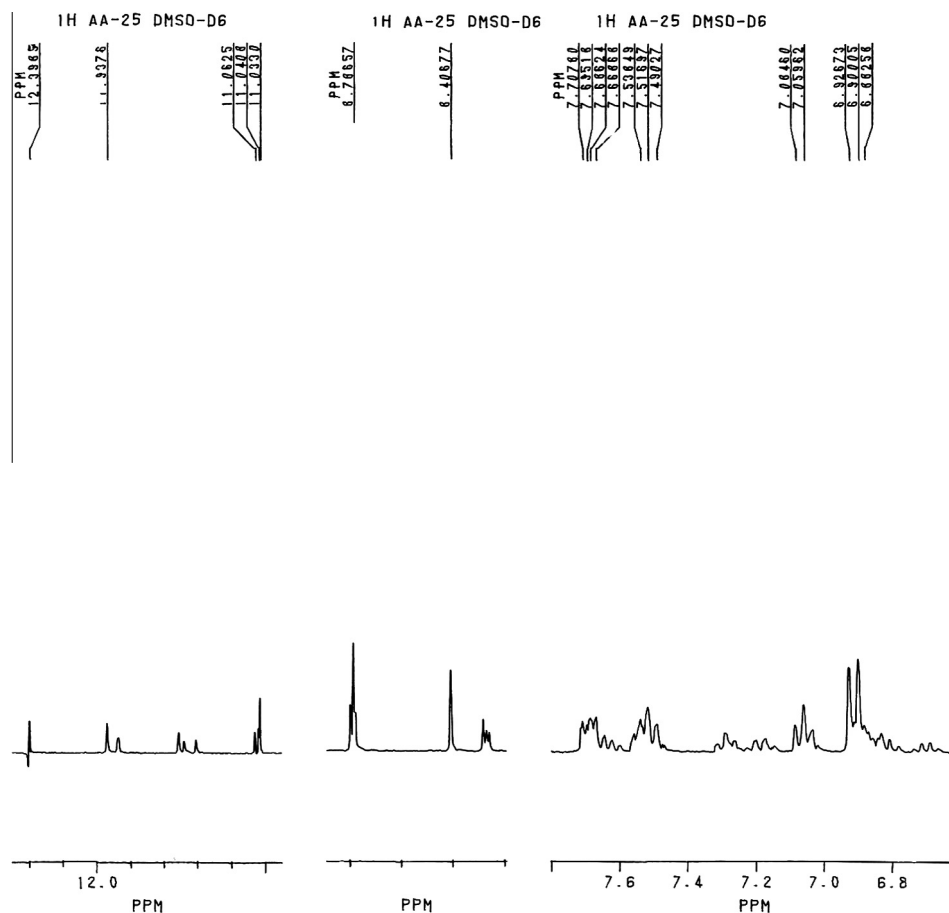


Fig. 5b. ^1H NMR Spectrum of the ligand in DMSO-d_6 (Amplified Form).

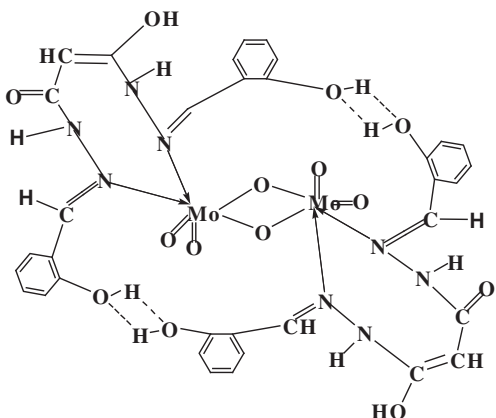
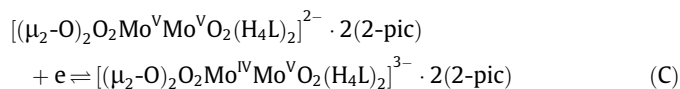
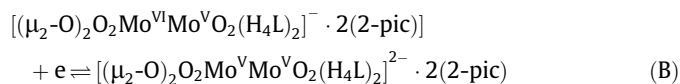
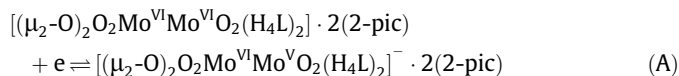


Fig. 6. Tentative structure Mo(VI) complexes $[(\mu_2\text{-O})_2(\text{MoO}_2)_2(\text{H}_4\text{L})] \cdot 2\text{A}$. Where $\text{H}_4\text{L} = \text{H}_4\text{slmh}$; $\text{A} = \text{H}_2\text{O}$ (1), py (2), 2-pic (3), 3-pic (4) and 4-pic (5).

(Fig. 4) since the ligand is inactive, it is quite plausible to suggest that these oxidations are predominantly metal centred $\text{Mo(VI)}/\text{Mo(V)}/\text{Mo(IV)}$ couples.

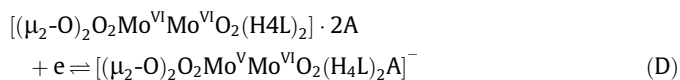
These couples are assigned to stepwise reduction of the $\text{Mo(VI)}/\text{Mo(VI)}$ to $\text{Mo(IV)}/\text{Mo(V)}$ and stepwise oxidation of the $\text{Mo(IV)}/\text{Mo(V)}$ to $\text{Mo(VI)}/\text{Mo(VI)}$. The redox couples are assigned to the following electron transfer reactions.



All the three complexes undergo three irreversible one-electron reductions which are successive $\text{Mo(VI)}/\text{Mo(V)}/\text{Mo(IV)}$ couples. The effect of the bridging ligand topology on the redox properties can be seen in the reductive and oxidative behaviour of these new complexes. However, the effect of the bridging ligand topology on the redox properties can be seen to be opposite in the oxidative behaviour of the complexes. However, it is difficult to explain why variation of the bridging ligand has such an opposite effect on the reductive and oxidative electrochemical behaviour. The most likely explanation is that although the reductions and oxidations are best described as formally metal-centred $\text{Mo(VI)}/\text{Mo(V)}/\text{Mo(IV)}$ couples [47], they are partly delocalized onto the 2-picoline molecule via a suitable π -symmetry orbital. There is, therefore, sufficient 2-picoline centred character of the oxidations. It is suggested that after the first electron transfer reaction (A) the 2-picoline molecule present in the lattice of the complexes enters into the coordination sphere around the molybdenum atom, it participates in redox reactivity by coordinating to the metal centre.

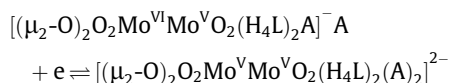
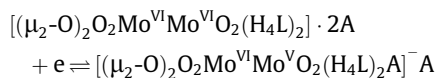
Further, the complexes (2) and (4) show only one reductive wave at -0.56 and -1.25 V and corresponding oxidative waves

at +0.44 and +0.59 V, respectively. These waves are assigned to the following redox reactions.




D = py(2), 3-pic(4)

Complex (5) shows two reductive and two corresponding oxidative waves. The essential features of these waves are that they have large separation reductive and oxidative waves suggesting that the high peak separation, most probably results from a slow heterogeneous electron exchange rate rather than from intervening heterogeneous reactions [48]. These waves are assigned to the following redox reactions



5. Conclusion

From the experimental evidences presented and discussed above that the ligand coordinates to the metal centre as a neutral bidentate ligand in keto enol form in all of the complexes. In the keto-enol form, the dihydrazone coordinate to the metal centre through azomethine nitrogen atoms only while carbonyl oxygen atoms remain free. The dihydrazone has *anti-cis* conformation in all of the complexes. The metal centres in these complexes are

bonded to one another by Mo  Mo bridging. In *anti-cis* con-

figuration both the azomethine nitrogen atoms are bonded to the same metal centre while the carbonyl oxygen remain uncoordinated. This introduces steric crowding in the molecule as a result of which the coordinated dihydrazone molecule is bent in such a way that one part remains in the equatorial plane while other one attain axial position. All of the complexes are suggested to have six coordinated distorted octahedral as shown in Fig. 6. The pyridine bases remain uncoordinated to the metal centre which is also supported by low frequency IR.

Acknowledgment

Authors are thankful to the Head, SAIF, North-Eastern Hill University, Shillong-793022, Meghalaya for CHN analyses and spectral studies.

References

- [1] O.A. Rajan, A. Chakravorty, *Inorg. Chem.* 20 (1981) 660.
- [2] M.M. Abu-omar, A. Loaiza, N. Hontzas, *Chem. Rev.* 105 (2005) 2227.
- [3] J. Topich, *Inorg. Chem.* 20 (1981) 3704.
- [4] E.I. Stiefel, *Science* 272 (1996) 1599.
- [5] R.H. Holm, *Coord. Chem. Rev.* 100 (1990) 183.

- [6] J.T. Spence, *Coord. Chem. Rev.* 48 (1983) 59.
- [7] J. Liimatainen, A. Lehtonen, R. Sillanpaa, *Polyhedron* 19 (2000) 1133.
- [8] C.P. Rao, A. Sreedhara, S. Venkateswara, P.V. Rao, N.K. Lokanath, M.A. Sridhar, J.S. Prasad, K. Rissanen, *Polyhedron* 18 (1999) 289.
- [9] M. Cindric, N. Strukan, V. Vrdoljak, B. Kamenar, Z. Anorg. Allg. Chemie 628 (2002) 213.
- [10] H. Arzoumanian, G. Agrifoglio, H. Krentzien, M. Capparelli, *J. Chem. Soc., Chem. Commun.* 1 (1995) 655.
- [11] H. Arzoumanian, L. Maurino, G. Agrifoglio, *J. Mol. Catal. A: Chem.* 117 (1997) 471.
- [12] M.M. Farahani, F. Farzaneh, M. Ghandi, *Catal. Commun.* 8 (2007) 6.
- [13] M.M. Farahani, F. Farzaneh, M. Ghandi, *J. Mol. Catal. A: Chem.* 248 (2006) 53.
- [14] K. Ambrozziak, R. Pelech, E. Milchert, T. Dziembowska, Z. Rozwadowski, *J. Mol. Catal. A: Chem.* 211 (2004) 9.
- [15] S.N. Rao, N. Kathale, N.N. Rao, K.N. Munshi, *Inorg. Chim. Acta* 360 (2007) 4010.
- [16] K.C. Gupta, A.K. Sutar, *Coord. Chem. Rev.* 252 (2008) 1420.
- [17] K.A. Jørgensen, *Chem. Rev.* 89 (1989) 431.
- [18] R.R. Schrock, A.H. Hoveyda, *Angew. Chem. Int. Ed.* 42 (2003) 4592.
- [19] M.H. Chisholm, in: M.H. Chisholm (Ed.), *Inorganic Chemistry: Towards the 21st Century*, ACS Symposium Series 211, American Chemical Society, Washington, DC, 1983, pp. 243–288.
- [20] J. Berg, R.H. Holm, *J. Am. Chem. Soc.* 106 (1984) 3035.
- [21] J. Berg, R.H. Holm, *J. Am. Chem. Soc.* 107 (1985) 917.
- [22] L.G. Hubert-Pfalzgraf, *New. J. Chem.* 11 (1987) 663.
- [23] J.M. Mitchell, N.S. Finney, *J. Am. Chem. Soc.* 1293 (2001) 862.
- [24] M.K. Trost, R.G. Bergman, *Organometallics* 10 (1991) 1172.
- [25] J. Belgacem, J. Kress, J.A. Osborn, *J. Am. Chem. Soc.* 114 (1992) 1501.
- [26] (a) A. Chakraborty, O.A. Rajan, *Inorg. Chem.* 20 (1981) 660; (b) M.M. Jones, *J. Am. Chem. Soc.* 81 (1959) 3188.
- [27] R.A. Lal, D. Basumatary, A.K. De, A. Kumar, *Transition Met. Chem.* 32 (2006) 481; R.A. Lal, J. Chakraborty, S. Bhaumik, A. Kumar, *Indian J. Chem.* 41A (2002) 1157; K.K. Narang, M.K. Singh, *Transition Met. Chem.* 12 (1987) 385.
- [28] R.A. Lal, S. Adhikari, A. Pal, A.N. Siva, A. Kumar, *J. Chem. Res. (M)* 749 (1997).
- [29] R.A. Lal, D. Basumatary, S. Adhikari, A. Kumar, *Spectrochim. Acta* 69 (2008) 706.
- [30] (a) M. Carcelli, S. Ianelli, P. Pelegghetti, G. Pelizzi, D. Rogolino, C. Solinas, M. Tegoni, *Inorg. Chim. Acta* 358 (2005) 369; (b) A. Bacchi, L.P. Bhattaghia, M. Carcelli, C. Pelizzi, G. Pelizzi, C. Solinas, M.A. Zoroddu, *J. Chem. Soc., Dalton Trans.* 773 (1993).
- [31] M.K. Singh, N.K. Kar, R.A. Lal, *J. Coord. Chem.* 61 (2008) 3158.
- [32] G.J.J. Chem, J.W. Mc Donald, W.E. Newton, *Inorg. Chem.* 15 (1976) 2612; O.A. Ranjan, A. Chakraborty, *Inorg. Chem.* 20 (1981) 660.
- [33] A.I. Vogel, *A Text book of Quantitative Inorganic Analysis*, Longman, London, 1973.
- [34] R.A. Lal et al., *Spectrochimica Acta Part A* 75 (2010) 212–224.
- [35] W.J. Geary, *Coord. Chem. Rev.* 7 (1971) 81.
- [36] (a) M.D. Cohen, S. Flavian, *J. Chem. Soc. B* 317 (1967) 329–334; (b) D. Gegiou, E. Lambi, E. Hadjoudis, *J. Phys. Chem.* 100 (1996) 17762; (c) T.N. Sorrell, *Tetrahedron* 54 (1989).
- [37] M. Hussain, S.S. Bhattacharjee, K.B. Singh, R.A. Lal, *Polyhedron* 10 (1991) 779.
- [38] D.G. Mc Collum, L. Hall, C. White, R. Ostrander, A.L. Rhenigold, J. Whelam, B. Bosnich, *Inorg. Chem.* 33 (1994) 924; E.I. Solomon, K.W. Penfield, D.E. Wilax, *Struct. Bonding (Berl.)* 53 (1983); Thapa, *Spectrochim. Acta* 50A (1994) 1005.
- [39] L.M. Jackman, *Resonance Spectroscopy in Organic Chemistry*, second ed., vol. 10, Pergamon Press, Amsterdam, 1978 (Chapter 3).
- [40] R.A. Lal, J. Chakraborty, A. Kumar, S. Bhaumik, R.K. Nath, D. Ghose, *Indian J. Chem.* 43A (2004) 516.
- [41] B. Ji, Q. Du, K. Ding, Y. Li, Z. Zhou, *Polyhedron* 15 (1996) 403.
- [42] J.K. Wu, B.P. Dailey, *J. Chem. Phys.* 41 (1965) 1849.
- [43] M. Nardelli, C. Pelizzi, G. Pelizzi, *Transition Met. Chem.* 2 (1977) 25.
- [44] W.P. Griffith, C.A. Pumphery, T.A. Rainey, *J. Chem. Soc. Dalton Trans.* 1125 (1986); V.V. Tkacher, L.O. Atovmyan, *J. Cord. Chem. (Engl. Transl)* 2 (1976) 89.
- [45] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, fifth ed. Part B., Wiley, New York, 1997. pp. 23, 56, 59.
- [46] N.C. Harden, E.R. Humphery, J.C. Jeffery, S.M. Lee, M. Marcaccio, J.A. Mc Cleverty, L.H. Rees, M.D. Ward, *J. Chem. Soc. Dalton Trans.* (1999) 2417.
- [47] S. Purohit, A.P. Koley, L.S. Prasad, D.T. Mauoharan, S. Ghosh, *Inorg. Chem.* 28 (1989) 3735 (and references thereof).
- [48] H. Okawa, M. Koikawa, S. Kida, *J. Chem. Soc. Dalton Trans.* (1988) 641.