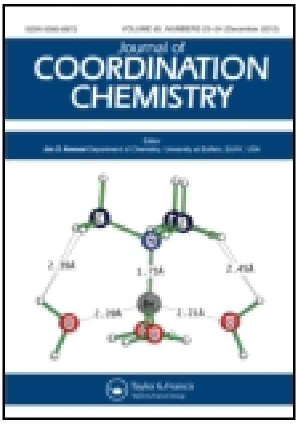

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Synthesis and characterization of molybdenum(V,VI) complexes derived from bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone

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Monometallic molybdenum(VI) complexes $[MoO_2(CH_2LH_2)]\cdot H_2O$ (**1**), $[Mo_2O_4(CH_2LH_2)_2(A)_2]$ (A = py (**2**), 2-pic (**3**), 3-pic (**4**) and 4-pic (**5**)) and molybdenum(V) complexes $[Mo(CH_2LH_2)(inh)]\cdot H_2O$ (**6**) and $[Mo(CH_2LH_2)(slh)]$ (**7**) of bis(2-hydroxy-1-naphthaldehyde) malonoyldihydrazone (CH_2LH_4) have been synthesized and characterized by various physico-chemical and spectroscopic studies. The compositions of the complexes have been established by elemental analyses and molecular weight determination. The structural assessment of the complexes has been done on the basis of data obtained from molar conductances, magnetic moment studies, electronic, infrared, electron paramagnetic resonance (EPR), proton nuclear magnetic resonance, and ^{13}C proton nuclear magnetic resonance spectroscopic studies. The molar conductance values for the complexes in DMSO suggest that they are non-electrolytes. The magnetic moment values for **6** and **7** correspond to one unpaired electron while the remaining complexes are diamagnetic. Complexes **1**, **6**, and **7** have six-coordinate octahedral stereochemistry around molybdenum, while **2**–**5** are eight-coordinate dodecahedral around the metal centers. EPR spectral features suggest that **7** is less symmetrical than **6**.

Keywords: Bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone; Molybdenum(VI,V) complexes; Isonicotinoylhydrazine; Salicyloylhydrazine; Magnetic moment and spectroscopic studies

1. Introduction

Molybdenum is the only element of the second transition series essential for life; as a constituent of enzymes it participates in redox reactions [1–3], catalyzing key reactions in nitrogen assimilation, amino acid catabolism, detoxification, and respiration.

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The biochemical role of molybdenum is based on its ability to facilitate electron exchange and to form stable complexes with nitrogen-, oxygen-, and sulfur-containing ligands [4, 5]. The useful role of molybdenum is not restricted to biological systems alone, but it also plays important roles in a variety of chemical reactions such as hydrodesulfurization, oxygen transfer, and olefin metathesis [6]. A number of catalytic oxygen atom transfer (OAT) systems involve mononuclear dioxomolybdenum(VI) and oxo-Mo(IV) complexes [7–11]. These systems are most notable for their reduction of dimethyl sulfide by oxo-Mo(VI) complexes [5–14]. OAT reactions form many $[MoO_2]^{2+}$ cores and proceed *via* multiple steps [12]. Basu *et al.* [12, 13] described the isolation and characterization of an intermediate of the OAT reaction, $LMoO(OPMe_3)Cl$ (where L = hydrotris(3,5-dimethyl-1-pyrazollyl)borate generated by reaction of $LMoO_2Cl$ with PMe_3). Hydrazone ligands can be used in the modeling of molybdenum-binding site of the molybdenum cofactor and that the steric factors are not absolutely essential to prevent Mo^V dimer formation with oxo-bridging. Another application of Mo(V), Mo(VI) species is in the synthesis of porous nanocapsules, which attracted attention as models for transmembrane cation transport [14]. Further, Mo(V) complexes having discrete molecularity are much less studied because their chemistry is dominated by binuclear species, where oxo-molybdenum(V) complexes consist of μ-oxo-($Mo_2O_3^{4+}$) and di-μ-oxo($Mo_2O_4^{2+}$) units. Only a few complexes of Mo(V) with Schiff bases are known [15–17]. While discharging its biochemical and catalytic functions, molybdenum cycles between +6 and +4 oxidation states *via* a +5 intermediate oxidation state [10]. Because of such importance of molybdenum, the coordination chemistry of mononuclear molybdenum(VI), (V), and (IV) complexes continues to attract a great deal of attention.

Despite considerable progress in the structural [18] and mechanistic [13] descriptions of these enzymes, fundamental chemical and electronic properties of molybdenum centers are poorly understood. Consequently, their impact on enzyme behavior is difficult to assess. Thus structural, spectroscopic, and chemical investigations of molybdenum complexes are fundamentally important for understanding the key centers in molybdo-enzymes and catalytic centers. The chemical information gained in studying molybdenum coordination complexes may be transferable to enzyme structure/functions and the catalytic center functions not readily studied.

Acyl-, aroyl-, and pyridoylhydrazones containing amide, azomethine, and phenol are polyfunctional ligands which react with metal ions either in the keto or the enol form [19]. Although a few complexes of metal ions with dihydrazones derived from condensation of salicylaldehyde and acyl-, aroyl-, and pyridoyldihydrazines have been reported, work done on dihydrazones containing active methylene functions and bulky naphthyl fragments in their molecular skeleton is virtually absent [20–24].

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 metal complexes of bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone (CH_2LH_4) (figure 1), molybdenum(V) and molybdenum(VI) complexes from the title dihydrazone have been synthesized and characterized, and the reactions of the resulting complex with electron and proton donors have been investigated. The resulting products from such reactions have been characterized by various techniques and spectroscopic studies and are reported in the present article.

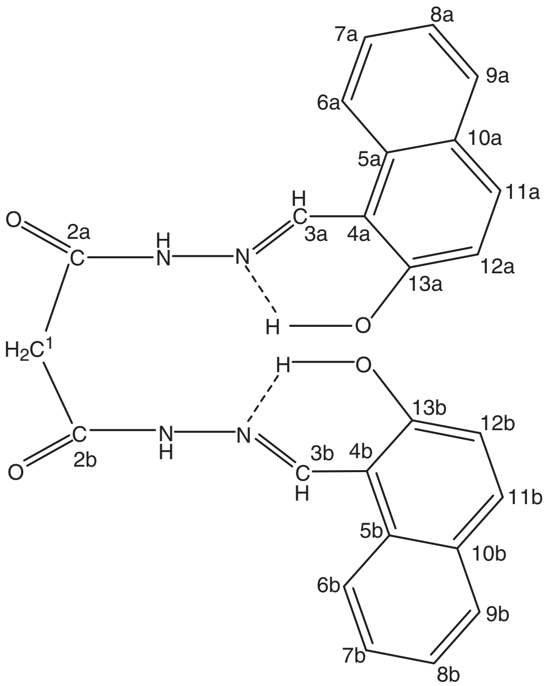


Figure 1. Structure and numbering scheme of bis(2-hydroxy-1-naphthaldehyde)malonoyl-dihydrazone (CH_2LH_4).

2. Experimental

2.1. *Materials and methods*

The metal salt, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, diethylmalonate, hydrazine hydrate, ethylsalicylate, and isonicotinoyl hydrazine were E-Merck or equivalent grade reagents. $MoO_2(acac)_2$ and salicyloylhydrazine were prepared by literature methods [25–27]. Malonoyldihydrazine was prepared by reacting diethyl malonate (1 mol) with hydrazine hydrate (2 mol). Bis(2-hydroxy-1-napthaldehyde)malonoyldihydrazone was prepared by reacting a warm dilute ethanol solution of malonoyldihydrazine (1 mol) with 2-hydroxy-1-naphthaldehyde (2 mol) and was suction filtered, washed with EtOH, and dried over anhydrous $CaCl_2$. Determination of molybdenum was carried by the standard literature procedure [28]. Carbon, hydrogen, and nitrogen were determined microanalytically on a Heraacus Carlo Erba 1108 microanalyzer. The molecular weights of the complexes were determined in DMSO by freezing point depression. Mass losses were determined by heating the complexes at 110°C, 180°C, and 220°C in an electronic oven. Thermogravimetric studies of the complexes were carried out on a Perkin-Elmer STA 6000 model in a ceramic crucible under dynamic dinitrogen. The heating rate of the samples was maintained at $20^\circ C\,min^{-1}$. The DTA standard used in the experiment is Pt10%Rh. APCI mass spectra of the complexes were recorded on a water ZQ 4000 Micromass Spectrometer. Room temperature magnetic susceptibility measurements were carried out on a model 155 PAR Vibrating Sample Magnetometer fitted with a Walker Scientific L75BAL magnet. Experimental magnetic susceptibility values have been corrected for diamagnetism by procedures given by Dutta and Syamal [29]. The molar conductances of the complexes at 10^{-3} mol L^{-1} in DMSO were measured on a Direct Reading Conductivity meter-303 with a dip type conductivity cell at room temperature. Infrared (IR) spectra were recorded on a Paragon 500 model IR spectrophotometer from 4000 to 350 cm^{-1} in KBr discs. The proton nuclear magnetic resonance (^{1}H NMR) and ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Varian EM-390, 90 and 25.16 MHz spectrometers in DMSO-d_6 using TMS as an internal standard. Electronic spectra of the complexes were recorded on a Milton Roy Spectronic-21 spectrophotometer. ESR spectra of the complexes in powdered form as well as in CH_3CN–DMSO solution at room temperature and liquid nitrogen temperature were recorded at X-band frequency on a Varian E-112 X1Q-band spectrometer using DPPH ($g = 2.0036$) as an internal field marker. Variable temperature experiments were carried out with a Varian Variable temperature accessory.

2.2. *Preparation of [$MoO_2(CH_2LH_2)$]•H_2O (1), [$Mo_2O_4(CH_2LH_2)_2(A)_2$] {where A = pyridine (py) (2), 2-picoline (2-pic) (3), 3-picoline (3-pic) (4), and 4-picoline (4-pic) (5)}*

Bis(acetylacetonato)dioxomolybdenum(VI) (0.68 g, 2.09 mmol) in ethanol (20 mL) was mixed with dihydrazone, H_4L (0.88 g, 2.00 mmol) in hot ethanol (30 mL). The resulting reaction mixture was stirred for 30 min at 70°C followed by refluxing for 3 h. The orange precipitate so obtained was filtered and washed with ethanol and ether and dried over anhydrous $CaCl_2$. Yield: 0.93 g.

Complex **2** was prepared by essentially the same procedure by adding pyridine (0.79 g, 10.00 mmol) to the solution obtained by mixing $MoO_2(acac)_2$ and dihydrazone at 1 : 1 molar ratio and refluxing the reaction mixture for 3 h. The yellow precipitate thus obtained was filtered, washed with ethanol and ether, and dried over anhydrous calcium chloride. Complexes **3**–**5** were prepared in the same manner using 2-picoline/3-picoline/4-picoline instead of pyridine.

2.3. *Preparation of [$Mo^V(CH_2LH_2)(inh)$]•H_2O (6) and [$Mo^V(CH_2LH_2)(slh)$] (7)*

[$MoO_2(H_2L)$] · H_2O (**1**) (0.58 g, 1.00 mmol) was taken in hot ethanol (80 mL) and stirred gently for 20 min to give a homogeneous suspension. This suspension was added to a solution of isonicotinoylhydrazine ($inhH_3$) (0.56 g, 6.00 mmol) in ethanol (30 mL) accompanied by gentle stirring. The resulting reaction mixture was refluxed for 1.5 h, which precipitated a dark-red compound. The compound was filtered, washed with ethanol and ether, and dried over anhydrous $CaCl_2$. Yield: 0.62 g.

Similarly, **7** was also prepared by using salicyloylhydrazine instead of isonicotinoylhydrazine. Yield: 0.43 g.

3. Results and discussion

The complexes described in the present article together with color, decomposition point, percentage yield, analytical data, magnetic moment, molar conductance, and electronic spectral data are given in table 1. The compositions of the complexes have been deduced based on data obtained from elemental analyses, thermoanalytical data, and molecular weight determinations. $[MoO_2(CH_2LLH_2)]\cdot H_2O$ (**1**), $[Mo_2O_4(CH_2LH_2)_2(A)_2]$ {where A = py (**2**), 2-pic (**3**), 3-pic (**4**), and 4-pic (**5**)}, $[Mo^V(CH_2LH_2)(inh)]\cdot H_2O$ (**6**), and $[Mo^V(CH_2LH_2)(slh)]$ (**7**) have been isolated.

The complexes are air stable and melt with decomposition at 242–270°C. Complexes **1**, **6**, and **7** have moderate solubility in CH_3CN, whereas the remaining complexes are only sparingly soluble in this solvent; all complexes are completely soluble in DMSO and DMF, but insoluble in water and common organic solvents like methanol, ethanol, acetone, benzene, ether, etc.

Molecular weights for the complexes were determined in DMSO by freezing point depression. The experimental values for **1**, **6**, and **7** are 540 ± 20, 650 ± 25, and 700 ± 30, respectively. These values are very close to the theoretical values calculated for monomers. The experimentally determined values for **2**–**5** are very close to the theoretical value calculated for dimers.

The molar conductance values for the complexes fall in the range 0.9–2.5 $Ohm^{-1}\,cm^2\,mol^{-1}$ at $10^{-3}\,mol\,L^{-1}$ in DMSO, suggesting non-electrolytes [30].

In order to establish the structures unequivocally with X-ray crystallography, an effort was made to crystallize the complexes in various solvent systems under different experimental conditions. Both saturated and dilute solutions of the complexes in various solvent systems (DMSO, DMF, DMSO–CH_3CN, DMSO–CH_2Cl_2, DMF–CH_3CN, and DMF–CH_2Cl_2) were kept for half, 1, and 2 months at ambient temperature to grow the crystals. Further, the solutions were gently evaporated at 40°C, 50°C, and 60°C in a hot electronic oven to promote crystal growth. After layering of a solution of the metal salts with a solution containing the ligand in ethanol was done, metal salts were also layered with a solution containing ligand in DMSO and DMF and metal salt solutions mixed with ligand solutions in DMSO and DMF were also layered with diethyl ether and the resulting solution in a small beaker was kept in a big beaker containing *n*-hexane. Unfortunately, in all our efforts only amorphous compounds precipitated, preventing analysis of the complexes by X-ray crystallography.

The μ_B values for **1**–**5** are zero, indicating molybdenum in +6 oxidation state with d° electronic configuration. Complexes **6** and **7** are paramagnetic, 1.60 and 1.65 BM, respectively, close to the spin-only value for a d^1 system. This is indicative of effective quenching of the orbital angular momentum by a low-symmetry ligand field surrounding the metal.

3.1. *Thermal studies*

All the complexes were heated at 110°C, 180°C, and 220°C in an electronic oven and weight loss was determined. None of the complexes showed weight loss at 110°C except **1** and **6** which showed weight loss corresponding to one water, suggesting a water in the lattice structure. Complexes **2**–**5** showed weight loss corresponding to one pyridine/2-picoline/3-picoline/4-picoline, respectively.

$[MoO_2(CH_2LH_2)]\cdot H_2O$ (**1**) and $[Mo_2O_4(CH_2LH_2)(2\text{-pic})]$ (**3**) were characterized by TGA studies as representative examples. The major decompositions occur in six prominent steps (Supplementary material). The first decomposition of **1** is at 123–186.50°C. After this, the complex remains stable until 225.9°C. The mass loss at

Table 1. Analytical, physico-chemical, and electronic spectral data of the complexes.

					Elemental analysis: Found (Calcd) %						Electronic spectral band λ_{max} (nm) ϵ_{max} ($dm^3\,mol^{-1}\,cm^{-1}$)	
	Complex/Color	Mol. Wt.	m.p.* (°C)	Yield (%)	Mo	C	H	N	μ_B (BM)	Molar conductance ($Ohm^{-1}\,cm^2\,mol^{-1}$)	CH_3CN	DMSO
1	$[MoO_2^{VI}(CH_2LH_2)]\cdot H_2O$ Orange	540 ± 20 (584)	270	80	16.01 (16.44)	51.88 (51.37)	3.38 (3.42)	9.00 (9.59)	–	2.5	320(9870) 400(7650)	330(10530) 395(8540) 490(56)
2	$[Mo_2O_4^{VI}(CH_2LH_2)_2(py)_2]$	1250 ± 50	242	75	14.54	56.20	3.60	11.21	–	1.2	340(10340)	330(8950)
	Yellow	(1290)			(14.88)	(55.81)	(3.57)	(10.85)			400(8760)	395(10230)
											500(10900)	510(280)
3	$[Mo_2O_4^{VI}(CH_2LH_2)_2(2\text{-pic})_2]$	1315 ± 45	250	76	14.23	55.97	3.75	10.95	–	0.9	325(9560)	330(10570)
	Yellowish orange	(1318)			(14.57)	(56.45)	(3.79)	(10.62)			390(10760)	400(13760)
											480(7340)	490(680)
4	$[Mo_2O_4^{VI}(CH_2LH_2)_2(3\text{-pic})_2]$	1300 ± 60	248	78	13.96	56.02	3.76	10.32	–	0.7	330(10500)	335(9270)
	Yellowish orange	(1318)			(14.57)	(56.45)	(3.79)	(10.62)			395(7650)	390(10250)

											450(9580)	460(10800)
5	$[Mo_2O_4^{VI}(CH_2LH_2)_2(4\text{-pic})_2]$	1310 ± 55	255	77	14.07	56.13	3.81	10.11	–	0.9	340(8760)	345(8380)
	Yellowish orange	(1318)			(14.57)	(56.45)	(3.79)	(10.62)			410(10880)	415(12730)
											490(6920)	500(790)
6	$[Mo^V(CH_2LH_2)(inh)]\cdot H_2O$	650 ± 25	248	62	13.48	54.78	3.39	14.71	1.60	2.1	350(10590)	390(8970)
	Dark-red	(686)			(13.99)	(54.23)	(3.50)	(14.29)			395(760)	430(9750)
											430(9890)	490(9230)
											500(5980)	640(390)
											635(350)	
7	$[Mo^V(CH_2LH_2)(slh)]$	700 ± 30	245	64	13.64	55.98	3.41	12.75	1.65	1.3	340(760)	380(8750)
	Dark-red	(683)			(14.06)	(56.22)	(3.37)	(12.30)			430(7380)	420(9390)
											500(8310)	490(8970)
											650(340)	650(330)

*Melts with decomposition.

123–186.5°C of 3.64% corresponds to loss of one water (theo: 3.08%). Although this water molecule is lost at considerably high temperature, it is suggested to be present in the lattice structure, clearly evident from the DTA curve of the complex which shows an endothermic peak centered at 167.5°C, suggesting that loss of water is a physical process.

The second mass loss is at 225–239°C of 10.38%, which corresponds to the loss of a part of the coordinated ligand. The DTA curve of the complex shows an exothermic peak with its center at 233°C. Subsequent to this, another mass loss from 239°C to 287°C is a relatively slow step with a relatively small mass loss of 13.11%, which corresponds to the loss of another fraction of the coordinated dihydrazone.

After 287°C, the complex shows an insignificant mass loss of 1% in a temperature interval of 20°C which is the fourth step. This mass loss process continues up to 543°C. After 543°C, a relatively faster mass loss occurs up to 797°C. The weight of the residue left at 797°C is 30.32, which is much higher than the percentage mass of MoO_3 (24.60%). This indicates that, at this temperature, a complex molybdenum species is formed from the combination of molybdenum, carbon, and oxygen. After 797°C, the weight of the substance remains almost constant until 812°C; however, an endothermic peak is observed in this region indicating a physical process, although it absorbs heat, suggesting that the complex either melts in this temperature range or undergoes phase change. The mass loss from 543°C to 797°C is about 2.5% at a temperature interval of 20°C which is much higher than the mass loss in the preceding step. The total mass loss from 543°C to 797°C is 30.56%. After 812°C, mass loss is still about 2.5% every 20°C, suggesting volatilization after 812°C.

Complex **3** shows thermal behavior similar to **1** but does not show any weight loss up to 200.3°C, ruling out water. The temperature ranges for decomposition steps occur at lower values in **3** than **1**. The decomposition ranges in **3** are 200.3–238.7, 238.7–289, 289–525.1, 538.5–767.2, and 789.6–890°C. The fact that decomposition ranges in **3** occur at lower values than in **1** suggest that **3** is more covalent than **1** from coordination of 2-picoline. The weight of residue at 890°C in **3** is 9.19%, while that in **1** is 18.90% at 892°C. However, after 797°C and 780.6°C in **1** and **3**, respectively, the weight never became constant to 900°C which prevents us from making an assessment of its composition.

3.2. *Mass spectra*

All of the complexes have been characterized by mass spectroscopy. The molecular ions along with the theoretical values of their average mass have been summarized in table 2. As molybdenum has six isotopes of roughly equal abundances, one peak in **1** and **2** appear in the form of four constituents, while in **6**, correspondingly three constituents are observed. Only **2** and **6** show two constituents around 628 and 707. The remaining peaks for all complexes appear as one peak only. Hence, the majority of the peaks in the present case may be regarded as an envelope of either two or more peaks because of isotopic mass distribution of molybdenum. Complexes **1**, **6**, and **7** show peaks characteristic of monomeric molecular ions. Complexes **1**, **6**, and **7** invariably show the presence of the molecular ion with one DMSO condensed with methylene of coordinated dihydrazone, e.g., $[MoO_2(CH_2LH_5)(DMSO)\{(DMSO)\text{-}(H_2O)\}]^+$(1) (707), $[Mo(CH_2LH_3)(inhH_3)\{(DMSO)\text{-}(H_2O)\}]^+$(8) (729), and

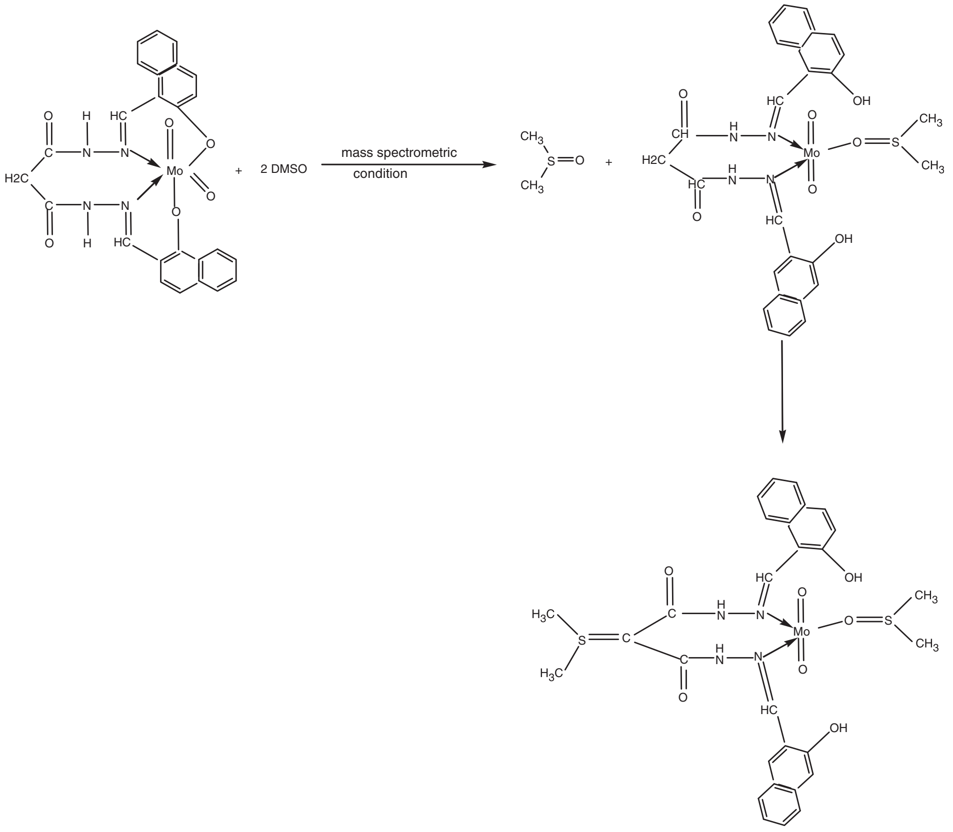
Table 2. Mass spectral data for the complexes.

Complexes	Molecular ion	Experimental mass		Theoretical mass
1	$[MoO_2(CH_5LH_2)(DMSO)_2]^+$	729.3	730.8	725
	$[MoO_2(CH_2LH_5)(DMSO)\{(DMSO)\text{-}(H_2O)\}]^+$	729.7	731.1	–
	$[MoO(CH_2L)(DMSO)\{(DMSO)\text{-}(H_2O)\}]^+$	707.4		707
	$[MoO_2(CH_2LH_2)]^+$	686.6		686
		564.3		567
2	$[(MoO_2)_2(CH_2LH_5)_2(py)(H_2O)\{(DMSO)\text{-}(H_2O)\}_2]$	1357.8		1355
		729.2	729.6	726
	$[MoO_2(CH_2LH_5)(py)(DMSO)]^+$	729.8	730.5	–
	$[MoO_2(CH_2LH_4)(py)\{(DMSO)\text{-}(H_2O)\}]^+$	707.3		707
	$[MoO_2(CH_2LH_4)\{(DMSO)\text{-}(H_2O)\}]^+$	628.3	628.2	628
3	$[Mo_2(CH_2LH_3)_2(2\text{-pic})_2]^+$	1256.1		1256
	$[Mo(CH_2LH_5)(DMSO)\{(DMSO)\text{-}(H_2O)\}]^+$	676.6		675
4	$[(Mo)_2(CH_2LH_3)_2(3\text{-pic})_2]^+$	1256.1		1256
	$[Mo(CH_2LH_5)(DMSO)\{(DMSO)\text{-}(H_2O)\}]^+$	676.6		675
5	$[(Mo)_2(CH_2LH_3)_2(4\text{-pic})_2]^+$	1256.1		1256
	$[Mo(CH_2LH_5)(DMSO)\{(DMSO)\text{-}(H_2O)\}]^{1+}$	676.4		675
6	$[Mo(CH_2LH_3)(inh)\{(DMSO)\text{-}(H_2O)\}]^+$	729.7		729
		730.5		–
	$[MoO_2(CH_2LH_5)(DMSO)\{(DMSO)\text{-}(H_2O)\}]^+$	731.0		707
		707.3		–
		707.8		–
7	$[Mo(slhH_3)(CH_2LH_5)(DMSO)\{(DMSO)\text{-}(H_2O)\}]$	831.6		827

$[Mo(slhH_3)(CH_2LH_5)(DMSO)\{(DMSO)\text{-}(H_2O)\}]^+$(7) (827), respectively. Complexes **2**–**5** show peaks characteristic of dimeric and monomeric molecular ions. Complex **2** shows a peak at 1357.8, which corresponds to the mass of $[(MoO_2)_2(CH_2LH_5)_2(py)(H_2O)\{(DMSO)\text{-}(H_2O)\}_2]^+$ (1355) with **3**–**5** showing similar mass spectral features. All of these complexes show a common ion at 1256.1, assigned to $[Mo_2(CH_2LH_5)_2(A)_2]^+$ (1256). In **2**–**5**, other peaks are observed at 707.3 and 676.6, assigned to $[MoO_2(CH_2LH_5)(py)\{(DMSO)\text{-}(H_2O)\}]^+$ and $Mo(CH_2LH_5)(DMSO)\{(DMSO)\text{-}(H_2O)]^+$, respectively. Similar to **1**, **6** and **7**, **2**–**5** show at least one molecular ion peak, which indicates condensation of dimethylsulfoxide with the methylene of the coordinated ligand as shown in scheme 1, in addition to the signal due to molecular ion containing uncondensed coordinated ligand. The mass spectral behavior suggests that **1**, **6**, and **7** are monomeric, while **2**–**5** are dimeric.

3.3. ^{1}H NMR spectra

Assignment of ^{1}H NMR spectra for CH_2LH_4 (table 3) has been made in light of literature [16, 20–22, 26]. The methylene protons appear as two signals at δ 3.90 and 3.60 ppm in the dihydrazones, indicating keto-enol equilibrium in solution [31]. The signal at δ 3.60 ppm is attributed to methylene protons ($–CH_2–$), that at δ 3.90 ppm is attributed to methine proton ($=CH–$). If the dihydrazone exists in the *syn-cis* configuration or staggered configuration, the OH, NH, and $–CH{=}N–$ resonances



Scheme 1. Reaction of molybdenum complexes in DMSO solution.

Table 3. ^{1}H NMR spectral data for the molybdenum complexes.

Complex/Ligand	δ(–CH$_2$–)	δ(Naphthyl)	δ(–CH=N–)	δ(OH)+ δ(NH)	Other signals
H$_4$L	3.90	8.30–7.03(m)	9.31(d, 32.90)	12.65(d, 63.00)	–
	3.60		8.60(d, 32.90)	11.50(d, 63.00)	
1	3.58	8.72–7.15(m)	9.80(d, 45.00)	12.46(d, 45.00)	–
			8.96(d, 45.00)	11.59(d, 45.00)	
2	3.77	8.47–7.00(m)	9.87(d, 38.71)	12.23(d, 61.20)	–
	3.46		9.11(d, 38.71)	11.15(d, 61.20)	
3	3.70	8.45–7.10(m)	9.76(d, 35.80)	12.40(d, 53.00)	2.45
	3.50		9.08(d, 35.80)	11.37(d, 53.00)	(2.55)[a]
4	3.64	8.58–7.08(m)	9.48(d, 32.40)	12.30(d, 49.50)	2.30
	3.52		9.14(d, 32.40)	11.24(d, 49.50)	(2.32)[a]
5	3.55	8.60–7.03(m)	9.61(d, 23.40)	12.35(d, 54.90)	2.07
			9.16(d, 23.40)	11.26(d, 54.90)	(2.32)[a]

[a] δ values for methyl protons for free substituted pyridine molecules.

each should appear as a singlet. However, the appearance of OH + NH and –CH=N– as doublets of doublets rules out the existence of the dihydrazone in staggered or *syn-cis* configuration, suggesting *anti-cis* configuration. The position of doublets is given in table 3 with coupling constant, "*J*" equal to 63 Hz for OH + NH protons and 32.9 Hz for azomethine protons.

The ^{1}H NMR spectra of **1–5** are similar to free dihydrazone. Four signals are observed from δ 12.80 to 10.77 ppm similar to free dihydrazone, two of which may be considered a doublet corresponding to equatorial and axial protons [32]. The resonances are weak and broad in the complexes as compared to free dihydrazone, indicating that they arise from secondary –NH protons [31]. The average position of these signals is upfield shifted by 0.41–0.09 ppm ruling out the possibility of involvement of secondary NH group in bonding. Such features of the ^{1}H NMR spectra in the OH + NH region indicate that the conformation of dihydrazone remains unaltered on complexation [22]. Similar to OH + NH resonances, –CH=N– signals also appear as four resonances in all complexes. The average –CH=N– shifts downfield by 0.72–0.37 ppm suggesting involvement of azomethine nitrogen in coordination. Another important feature of ^{1}H NMR spectra of the complexes is the upfield shift shown by methylene protons (3.80–3.46 ppm), although the possibility of interference with these signals due to water absorbed by DMSO-d_6 cannot be ruled out. This signal shifts upfield by 0.20–0.11 ppm indicating increase in electron density on methylene, further ruling out the possibility of involvement of >C=O in coordination. This evidence indicates that N_2O_2 coordination in the complexes [33] is possible only if the dihydrazone coordinates to metal in the *anti-cis* configuration.

Methyl has signals at δ 2.55, 2.32, and 2.37 ppm in free 2-picoline, 3-picoline, and 4-picoline, respectively [31]. In **3–5**, these signals appear at δ 2.45, 2.30, and 2.07 ppm, respectively, and are thus upfield shifted from the removal of electron density from ring nitrogen to the metal, causing decrease in electronegativity of ring nitrogen [22]. These complexes do not show a signal downfield which can be assigned to pyridinium or 2-picolinium or 3-picolinium or 4-picolinium ions [34].

3.4. *^{13}C NMR spectroscopy*

Only **4** has been characterized by ^{13}C NMR spectroscopy. The chemical shift δ (ppm from $SiMe_4$) and the chemical shift changes $\Delta\delta$ (ppm) accompanying the coordination of the ligand are shown in "Supplementary material". Assignments for the ligand have been deduced taking into account the shift in resonances of naphthyl ring carbon caused by the azomethine and naphtholic –OH. The numbering scheme for carbons in both ligand and complex are shown in figure 1. Carbons in the axial and equatorial positions have been designated by the letters "a" and "b", respectively.

As a result of coordination many signals are split resulting in more signals than in the free ligand. Metal ions shift carbon resonances of naphthyl ring downfield, C(6), C(8), and C(9) by at least 0.10–0.60 ppm, respectively. Signals due to C(7) and C(11) show an upfield shift by 0.02–1.05 ppm, respectively. Signals due to C(2), C(4), and C(12) remain unshifted or shift upfield by 0.10–5.85 ppm. The non-shifting or shift to higher field of C(2) rules out the possibility of coordination of >C=O to metal. It is, therefore, reasonable to expect that C(13) and C(3) shift downfield even more since they are closer to the coordinated oxygen and nitrogen. As a consequence, the signal for C(13) (in free ligand at δ 157.8 and 156.7 ppm) could either be at δ 157–152.2 or at δ 171–169 ppm in **4**. The latter assignment is more likely since it gives a deshielding of δ 14.35–11.9 ppm, whereas the former assignments only give shielding of 2.50 ppm in **4**. Thus the signal at δ 157.8–152.2 can only be assigned to the azomethine carbon, C(3), giving a chemical shift change of δ 11.97–8.95 ppm. The δ 146.0–143.0 ppm could be assigned to C(10), while those at δ 135.9–131.45 ppm to C(5) carbon. These carbons absorb at δ 142.9, 142.5 and 132.3, 132.4 ppm, respectively, in free dihydrazone. The signal at δ 121.0–120.2 ppm is assigned to C(4a) and C(4b), which in free ligand are at δ 121.0 and 120.8 ppm giving an upfield shift of 0.10 ppm in **4**.

In view of the above spectral features and discussions of the ^{13}C NMR spectra of the complex, it is reasonable to suggest that the ligand and metal complexes have the same symmetry and that the dihydrazone is coordinated to the metal in *anti-cis* configuration [33].

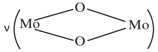
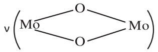
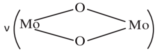
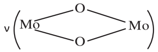
New signals have been observed in the ^{13}C NMR spectrum of **4** (given in table 3) which are not present in the spectrum of free ligand, assigned to various carbons of 3-picoline. A comparison of the positions of various carbons in **4** with those in free 3-picoline shows that they are all upfield shifted which suggests coordination of 3-picoline.

3.5. *IR spectra*

The ligand shows strong broad bands at 3450, 3200, and 3047 cm^{-1}, assigned to stretching vibrations of naphtholic –OH and secondary –NH [23, 24, 31]. IR spectra of the complexes show either medium or strong bands at 3300–3550, 3184–3212, and 3027–3105 cm^{-1}, except **6** which shows a strong broad band at 3000–3550 cm^{-1}. IR spectra of the complexes are complicated in the region 3000–3550 cm^{-1} because of bands due to the stretching vibrations of secondary –NH and salicyl –OH in **7** and possible water in KBr pellets. In order to decide whether bands in this region arise from H_2O present either in lattice or absorbed by KBr pellets, the compounds were heated at 110 and 180°C, respectively, and the ensuing vapor identified by passing through a trap containing anhydrous $CuSO_4$. Thus, **2**–**5** and **7** showed no weight loss at 110°C or 180°C, indicating that in these complexes, bands at 3550–3300 cm^{-1} arise due to moisture absorbed by KBr pellets. However, in **7** the band arises due to joint contribution from coordinated salicyl –OH and water absorbed by KBr pellets. The essential features of the band at 3212 cm^{-1} in **7** compared with **6** suggest involvement of salicyl –OH of salicyloylhydrazine in hydrogen bonding [35]. Complexes **1** and **6** show weight loss at 110°C and ensuing gas turned anhydrous $CuSO_4$ blue, indicating that the bands in these complexes at 3550–3000 cm^{-1} have contribution from lattice water. Complexes **2**–**5** show a distinct band due to νNH at 3184–3212 cm^{-1} as in free dihydrazone. The νNH remains almost unshifted in the complexes dismissing the possibility of coordination of secondary NH to the metal.

The amide I bands are at 1697 and 1661 cm^{-1} in free dihydrazone, but fall in the region 1669–1671 cm^{-1} (table 4) in the complexes, suggesting non-coordination of >C=O. In the coordinated dihydrazone, the >C=O group is more strongly H-bonded than in the free state as shown by X-ray crystallography by Pelizzi *et al.* [23]. The strong band at 1532 cm^{-1} is assigned to have composite character due to contribution of the amide II and ν(C–O) (naphtholic). This band shifts to higher frequency by 2–8 cm^{-1},

Table 4. IR spectral data for the molybdenum complexes.

Complex	ν(OH)+ ν(NH)	Amide I ν(C=O)	ν(>C=N–N=C<)	Amide II + ν(C=O)	β(C–O) (naphtholic)	ν(N–N)	$\nu(MoO_2^{2+})$	ν(M–O) (naphtholic)	Others
H_4L	3450sbr 3200s 3047s	1697vs 1661vs	1617vs 1596vs	1532vs	1278s	1030w	–	–	–
1	3345s 3184s	1669s	1616s 1595s	1557s	1280m	1033w	938vs 910vs	591s	–
2	3345s 3189s 3095s	1669s	1620s 1602s	1539s	1280m	1032w	938s 910s 850vs	592w	1080w (py) 735s 
3	3350s 3200s	1670s	1618s 1598s	1540s	1282m	1038w	940s 915s 848vs	593w	1070w (2-pic) 733ssh 
4	3400s 3185s 3105s	1669vs	1619s 1593s	1537s	1280m	1032w	951s 905s 856s	–	1075w (3-pic) 738s 
5	3421s 3184s 3105s	1669s	1619s 1593s	1535s	1280m	1033w	933s 916s 854vs	–	730ssh 
6	3500- 3000sbr	1671s	1618s 1594s	1534s	1272s	1057w	–	–	1504s ν(N=N)
7	3395s 3212s	1669s	1614s 1596s	1535s	1274s	1031w	–	591w	1481s ν(N=N)

ruling out the possibility of involvement of >C=O in bonding. However, it suggests involvement of naphtholic (C–O) in bonding. Purohit *et al.* [35a] and Syamal and Kale [35b] have shown that the shift of ν(C–O) (phenolic/naphtholic) to higher frequency indicates involvement of phenolic/naphtholic (C–O) group in bonding to the metal. This suggests flow of naphthyl ring electron density to the metal center through naphtholate oxygen [35].

The ligand shows very strong bands at 1617 and 1596 $\mathrm{cm^{-1}}$ assigned to νC=N. In all of the complexes, this band is similar with one component at 1614–1620 $\mathrm{cm^{-1}}$ and the second at 1593–1602 $\mathrm{cm^{-1}}$. The average νC=N shifts to higher frequency by 4 $\mathrm{cm^{-1}}$ in **2** while in the remaining complexes it remains almost unshifted, indicating νC=N has different bonding (H^+ or M^{2+}) [35, 36].

The new band at 570–550 $\mathrm{cm^{-1}}$ is assigned to ν(M–O) (naphtholic) [34]. Complexes **2**–**5** show bands at 660–685 and 440–435 $\mathrm{cm^{-1}}$ assigned to in-plane ring deformation and out-of-plane ring deformation of pyridine/2-picoline/3-picolin3/4-picoline. These bands are considerably shifted compared to free pyridine/2-picoline/3-picolin3/4-picoline molecules, indicating coordination of pyridyl ring nitrogen [37].

Complexes **1**–**5** show two bands at 905–951 $\mathrm{cm^{-1}}$ indicating *cis* oxo's, with 933-951 $\mathrm{cm^{-1}}$ assigned to symmetric stretch and 902–916 $\mathrm{cm^{-1}}$ to antisymmetric stretch. The intensity of both $\nu\mathrm{MoO_2^{2+}}$ bands in **1** is very high, whereas in **2**–**5**, the intensity of one band is reduced compared to **1**. Complexes **2**–**5** show a strong to very strong band at 848–856 $\mathrm{cm^{-1}}$. Two bands at 905–951 $\mathrm{cm^{-1}}$ coupled with a band at 848–856 $\mathrm{cm^{-1}}$ suggest bridging $\mathrm{Mo{=}O\cdots Mo}$ [19, 21, 25] is moderately strong, but maintains its identity as *cis*-$\mathrm{MoO_2^{2+}}$. Thus a dimeric structure with $\mathrm{Mo{=}O\cdots M}$ may be suggested in **2**–**5**. Complexes **2**–**5** show a new band at 730–738 $\mathrm{cm^{-1}}$, similar to those observed by Griffith *et al.* [38], Holm *et al.* [39], and other workers [19] and is assigned to ν(Mo–O–Mo). This typical band at 730–738 $\mathrm{cm^{-1}}$ suggests bridging (Mo–O–Mo) in the complexes.

Complexes **6** and **7** show IR spectral features different from **1–5**, with the absence of any band characteristic of >C=O and NH_2 at 1660–1630 $\mathrm{cm^{-1}}$ and ν(Mo=O) at 1000–850 $\mathrm{cm^{-1}}$. Complexes **6** and **7** show a strong band at 1506 and 1482 $\mathrm{cm^{-1}}$, respectively, characteristic of (N=N) [40]. All these features suggest condensation of –NH_2 of the hydrazides with Mo=O, enolization of >C=O, and inclusion of salicyloyl- and pyridoyldiazenido in the molybdenum coordination sphere. The paramagnetic **6** and **7** precluded recording their ^{1}H NMR spectra. As a result, these suggestions remain tentative only. Weak bands at 2800 $\mathrm{cm^{-1}}$ in the IR spectrum of free $\mathrm{sylshH_3}$ attributed to intramolecular H-bonding between >C=O and –OH groups disappears in **7**. However, a well-defined broad band at 3217 $\mathrm{cm^{-1}}$ different from **6** suggests intermolecular H-bonding between salicyl –OH from different complexes [41].

3.6. *Electronic spectra*

Important electronic spectral bands for $\mathrm{CH_2LH_4}$ and complexes isolated in the present study along with molar extinction coefficients are given in table 1. The free $\mathrm{CH_2LH_4}$ shows bands at 320 and 390 nm, 320 nm is assigned to intraligand $n\rightarrow\pi^*$ transition, while 390 nm is assigned to $\pi\rightarrow\pi^*$ transition. The band at 390 nm characteristic of naphthaldimine has been reported in several monoacylhydrazones [11].

Electronic spectra for the complexes show two to four bands in the 330–500 nm regions. The ligand bands at 320 and 390 nm red shift on complexation. Bands at 330–370 nm are attributed to ligand band at 320 nm and bands at 390–430 nm to ligand band at 390 nm. The red shift gives evidence of chelation of dihydrazone to the metal center [26, 36]. The magnitude of shift of ligand bands on complexation indicates strong bonding between the ligand and the metal center. Electronic spectra of all the complexes are dominated by a new strong charge-transfer band at 330–540 nm indicative of discrete molecularity [42]. All of the complexes show a new band at 430–490 nm with a very high molar extinction coefficient, assigned to ligand-to-metal charge transfer [43]. This band probably arises from charge-transfer transition from naphtholate oxygen to the metal [43]. This ligand-to-metal charge-transfer band which is strongly influenced by the chemical nature of the ligand within a given stereochemistry is responsible for the color of the complexes. These complexes do not show any band in the visible region which could be assigned to either Mo(V) or Mo(IV), consistent with the presence of Mo(VI) in these complexes.

The Mo(V) complexes **6** and **7** show a distinct weak band at 640 and 650 nm assigned to the first crystal field transition $^2B_2 \rightarrow {}^2E$ ($d_{xy} \rightarrow d_{xz}$, d_{yz}). The second crystal field transition $^2B_2 \rightarrow {}^2B_2$ ($d^2_{xy} \rightarrow x^2 - y^2$) is obscured either by strong ligand band at 430 nm or charge-transfer transition occurring at 490 nm. The high molar extinction coefficient for the band at 640 nm in these complexes indicates that the band might have borrowed some intensity from allowed charge-transfer band. The d–d bands remain almost unshifted in position in DMSO solution which rules out the possibility of interaction of solvent to the metal center.

3.7. *Electron paramagnetic resonance spectroscopy*

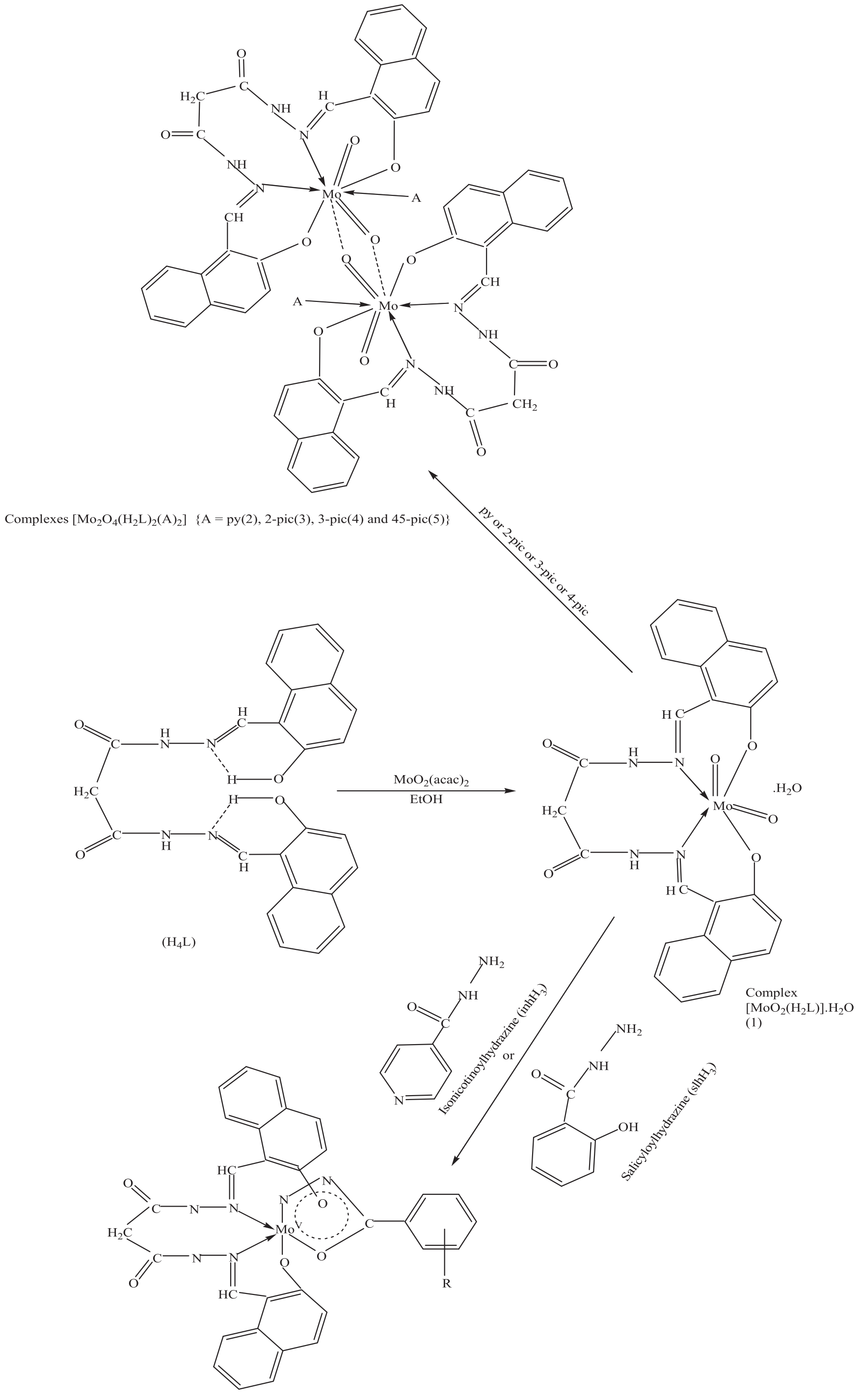
The Mo(V) complexes **6** and **7** (Supplementary material) have been characterized by electron paramagnetic resonance (EPR) spectroscopy in the solid state. Both show anisotropic spectra (table 5). However, there are significant differences dependent upon the type of ligand coordinated to molybdenum.

The spectrum of **6** is split into $g_{\parallel} = 2.111$ and $g_{\perp} = 1.933$. Such a spectrum can be explained by assuming axial symmetry. The satellite peaks ($A = 70$ G and $A = 80$ G) are due to ^{95,97}Mo (25.15 atom %, $I = 5/2$). The derived g and A tensor components indicate that the unpaired electron is located in a molybdenum-centered orbital.

The spectrum of **7** is consistent with rhombic symmetry with $g_1 = 2.053$, $g_2 = 1.993$, and $g_3 = 1.915$. The symmetry determines the allowed intermixing of metal d-orbitals which can result in significant non-coincidence of the principal axes of the g and A tensor. The point group symmetry of **7** cannot be higher than C_1. The anisotropic nature of the spectrum indicates the highly unsymmetrical structure, resulting in a

Table 5. Magnetic parameters for molybdenum(V) complexes.

Complex	Temperature (state)	g_{av}	g_1 or $g_{\parallel}$	g_2	g_3 or $g_{|}$	A_{av}	A_1 or $A_{\parallel}$ (G)	A_2 (G)	A_3 or $A_{|}$ (G)
6	LNT (Solid)	1.995	2.111	–	1.933	76.7	70	–	80
7	LNT (Solid)	1.987	2.053	1.993	1.915	40	40	40	40



Complexes $[Mo_2O_4(H_2L)_2(A)_2]$ {A = py(2), 2-pic(3), 3-pic(4) and 45-pic(5)}

(H_4L)

Complex
$[MoO_2(H_2L)].H_2O$
(1)

$[Mo^V(CH_2LH_2)(inh)].H_2O$ (6) $[Mo^V(CH_2LH_2)(slh)]$ (7)

Scheme 2. Synthesis of molybdenum complexes.

significant difference in the EPR spectral features as compared to that of **6**. This may be related to involvement of salicyl –OH in H-bonding rather than the nature of the chelate skeleton that is primary for dictating difference in the EPR spectra. Fairly high values of $\langle g \rangle$ and $\langle A \rangle$ are in conformity with the oxygen and nitrogen coordination in these compounds [44].

4. Conclusions

The experimental evidence shows that **1**, **6**, and **7** are monomeric while **2**–**5** are dimeric. The dihydrazone coordinates to metal in keto form as a dibasic ligand in *anti*-*cis* configuration. In **1**, molybdenum is six-coordinate octahedral, while in **2**–**5** it is eight-coordinate dodecahedral stereochemistry. In **1**, both the azomethine nitrogen and one naphtholate oxygen of the dihydrazone are equatorial, while the second naphtholate oxygen occupies the axial position. Both oxo of MoO_2^{2+} group are *cis*; one is equatorial while the other is axial. In **2**–**5**, the dihydrazone remains essentially the same as in **1** with the remaining positions occupied by oxo-oxygen, bridged oxo-oxygen, and pyridyl ring nitrogen of pyridine/2-picoline/3-picoline/4-picoline, respectively. Complexes **6** and **7** do not contain oxo-groups. The $-NH_2$ of salicyloylhydrazine and isonicotinoylhydrazine condense with MoO_2^{2+} accompanied by an eventual reduction of the metal center. For **6** and **7**, six-coordinated octahedral stereochemistry is proposed with the diazenido group spanning the positions originally occupied by oxo-oxygens.

Tentative structures for the complexes are shown in scheme 2.

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