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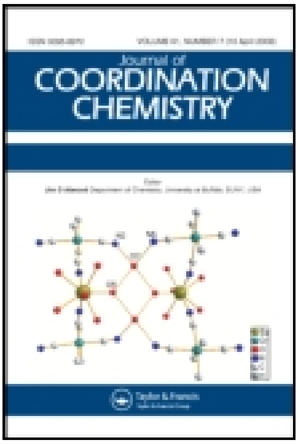

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Synthesis and spectral characterization of homobimetallic molybdenum(VI) complexes derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

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The reaction of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone with bis(acetylacetonato)dioxomolybdenum(VI) ($MoO_2(acac)_2$) in 1 : 3 molar ratio in EtOH : water mixture (95 : 5) affords a complex of composition $[(MoO_2)_2(nsh)(H_2O)_2] \cdot C_2H_5OH$. The reaction of $[(MoO_2)_2(nsh)(H_2O)_2] \cdot C_2H_5OH$ with Lewis bases, namely pyridine, 2-picoline, 3-picoline, and 4-picoline, yields $[(MoO_2)_2(nsh)(B)_2] \cdot C_2H_5OH$ (where B = pyridine, 2-picoline, 3-picoline, and 4-picoline). Further, when this complex was reacted with 1,10-phenanthroline and 2,2′-bipyridine in 1 : 3 molar ratio in anhydrous ethanol the binuclear complexes $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(phen)] \cdot C_2H_5OH$ and $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(bpy)] \cdot C_2H_5OH$ were obtained. All of the complexes have been characterized by analytical, magnetic moment, and molar conductivity data. The structures of the complexes have been discussed in the light of electronic, IR, ^{1}H NMR, and ^{13}C NMR spectroscopy.

Keywords: Molybdenum(VI); Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone; Homobimetallic; Spectroscopic studies

1. Introduction

Molybdenum functions as a heterogeneous catalyst for the oxidation of organic compounds in high oxidation states. Homogeneous oxo-transfer chemistry of MoO_2^{2+} is known to be biomimetic [1].

Research in molybdenum complexes is mainly due to its biochemical role in metalloenzymes [2] and rather complex chemistry. Molybdenum is the only element of the second transition series essential for life; as a constituent of enzymes it participates in redox reactions, e.g., oxidation of aldehydes, xanthine, and other purines [3], and reduction of nitrate to molecular nitrogen [4, 5]. Molybdenum's biochemical role is based on its ability to facilitate electron exchange and to form stable complexes with oxygen, nitrogen, and sulfur containing ligands. The useful role of molybdenum is not

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only restricted to biological systems, but also plays important roles in a variety of chemical reactions such as hydrodesulfurization, oxygen transfer reactions (e.g., olefin epoxidation), and olefin metathesis. The *cis*-dioxo compounds displaying catalytic activities [6] are models for enzymes [7, 8] and are useful material precursors [9]. Catalytic activity is frequently linked to coordinative unsaturation and the active sites in various molybdenum oxidation catalysts are believed to contain coordinatively unsaturated molybdenum centers [10–12]. In all of these biological and industrial reactions, molybdenum plays the role of a catalytic redox site. Molybdoenzymes consist of two Mo atoms per molecule, suggesting binuclear Mo-sites joined by one or two oxo- or sulfido-bridges [13].

Close proximity of metal ions in multimetallic complexes considerably varies the properties of the system which may be significantly different from properties of monometallic complexes. Homomultimetallic complexes have the potential to mediate chemical reactions of industrial relevance either more efficiently than, or in a different manner to, monometallic complexes. They exhibit distinct reactivity patterns compared to corresponding monometallic complexes [14]. As a result, synthesis and characterization of homobimetallic complexes continue to attract attention [15]. Especially, the role of *cis*-MoO_2^{2+} in metalloenzymes has led to studies of complexes with ligands containing nitrogen, sulfur, or oxygen donors and the analysis of their chemical, spectroscopic, and structural properties [16].

A survey of literature reveals that although metal complexes of Schiff bases derived from the condensation of a variety of aldehydes and ketones with several aliphatic and aromatic amines have been studied in detail [17, 18], metal complexes of Schiff bases derived from monoacyl-, aroyl-, and pyridoyl-hydrazines have been studied to much less extent [19–24]. Further, there are reported dicopper complexes of multihydrazones [25] and molybdenum complexes of thiosemicarbazones [26]. Moreover, although a few homobimetallic complexes of salicylaldehyde, *o*-hydroxy aromatic aldehyde, and ketone dihydrazones with first series transition metal ions have been synthesized and characterized [27–31], those derived from dihydrazones having bulky fragments in their molecular skeleton have received scant attention [32, 33].

In view of the importance of multimetallic complexes and much less work on the multimetallic complexes of the dihydrazones containing bulky fragments in their molecular skeleton, it was of interest to synthesize homobimetallic complexes of the title dihydrazone and characterize the resulting products by various physico-chemical and spectral techniques. Accordingly, the present article describes the synthesis and characterization of homobimetallic complexes of Mo(VI) derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh) (figure 1) in ethanolic media and their characterization by various physico-chemical techniques and spectroscopic methods.

The numbering scheme of the carbons in the ligand and the complexes are shown in figure 1 and figure S1 in "Supplementary material". The carbons in axial and equatorial positions have been designated by the letters "a" and "b", respectively [33].

2. Experimental

Ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), diethyl succinate ($(CH_2)_2(CO_2Et)_2$), hydrazine hydrate ($N_2H_4 \cdot H_2O$), and 2-hydroxy-1-naphthaldehyde ($C_{10}H_6(OH)(CHO)$

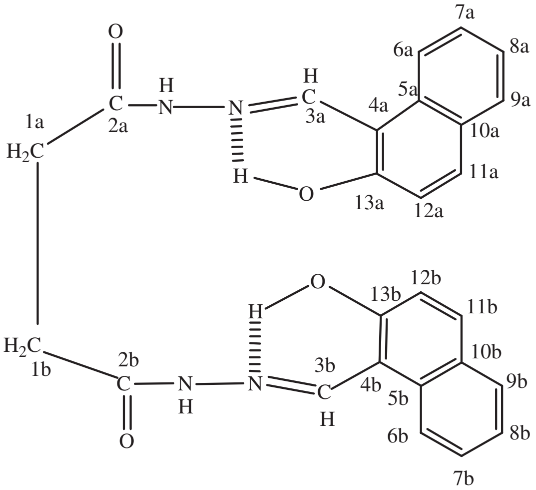


Figure 1. Structure along with numbering scheme of H_4nsh.

were of E-Merck, Qualigens, Hi-Media or equivalent grade reagents and were used without purification. Acetyl acetone, pyridine, 1-picoline, 2-picoline, 3-picoline, and 4-picoline were Lanchaster or equivalent grade reagents. The solvents ethanol, methanol, diethyl ether, dimethyl sulfoxide (DMSO), and dimethyl formamide (DMF) were used after purification by standard literature methods. Bis(acetylacetonato) dioxomolybdenum(VI) ($MoO_2(acac)_2$) was prepared by the literature method [34].

2.1. *Analysis of the complexes*

Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHNS/O Analyzer 11. Water, ethanol, pyridine, 3-picoline, and 4-picoline were determined from the percentage weight losses obtained by heating the samples in the temperature range 60–250°C. The detailed thermal analyses of **1**, **2**, **4**, and **5** in the temperature range 60–250°C were carried out. The samples were heated manually at each of the temperatures (60, 65, 70, ..., 250°C) for half an hour. The weight loss was determined by subtracting the weight of the complex obtained after heating from the weight of the complex before heating, and thus the weight losses and percentage weight losses were calculated. Molybdenum content of the complexes was determined by the standard literature procedure [35].

2.2. *Physical measurements*

Molar conductance of the complexes at 10^{-3} M in DMSO was determined using a Wayne Kerr B 905 Automatic Precision Bridge with a dip-type conductivity cell. Infrared spectra from 4000 to 400/500 cm^{-1} were obtained on either a BX-III/FT-IR Perkin–Elmer spectrophotometer or a Nicolet-Impact 410 FT-IR spectrophotometer as KBr discs. Electronic spectra of the ligand and complexes in DMF were recorded on a Perkin–Elmer Lambda 25 spectrophotometer at 10^{-3} M. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-F 300 MHz and AMX 400 High-Resolution Multinuclear FT-NMR Spectrometer in DMSO-d_6. Tetramethylsilane (TMS) was used as an internal standard.

2.3. *Preparation of the ligand*

Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone was prepared in two steps. In the first step, succinoyldihydrazine (SDH) was prepared by reacting diethyl succinate with hydrazine hydrate in 1 : 2.5 molar ratio. In the second step, SDH (1.00 g, 6.84 mmol) was allowed to react with 2-hydroxy-1-naphthaldehyde (2.59 g, 15.04 mmol) in 1 : 2.2 molar ratio in ethanol under reflux for 30 min. The yellow precipitate thus obtained was purified by washing with hot ethanol and dried over anhydrous $CaCl_2$. The m.p. was 254°C (Anal.: Found(%): C, 68.81; H, 4.80; and N, 12.65). Required for $C_{26}H_{22}O_4N_4$(%): C, 68.72; H, 4.84; and N, 12.33.

2.4. *Preparation of* $[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ *(1)*

The dihydrazone ligand (H_4nsh) (1.00 g, 2.20 mmol) was suspended in ethanol : water mixture (100 mL (95 : 5)) and stirred for 30 min at 70°C. A solution of bis(acetylacetonato)dioxomolybdenum(VI) ($MoO_2(acac)_2$) (2.15 g, 6.59 mmol) in ethanol (50 mL) for molar ratio 1 : 3 was added to this. The reaction mixture was refluxed for 3 h which yielded an orange precipitate. The product was filtered hot, washed several times with hot ethanol and then with ether, and dried over anhydrous $CaCl_2$. Yield: 0.66 g.

2.5. *Preparation of* $[(MoO_2)_2(nsh)(B)_2]\cdot C_2H_5OH$ *(where B = pyridine (py, 2); 2-picoline (2-pic, 3); 3-picoline (3-pic, 4); 4-picoline (4-pic, 5))*

Complex **1** (1.00 g, 1.27 mmol) was suspended in ethanol (100 mL) accompanied by gentle stirring for 15 min at 60–70°C. Pyridine (1.02 mL, 12.64 mmol) was added (molar ratio 1 : 10) to this suspension. The reaction mixture was refluxed for 3 h which precipitated a yellowish-orange compound. The compound thus obtained was filtered and collected. Yield: 0.7 g.

Complexes **3**–**5** were prepared similarly using 2-picoline, 3-picoline, and 4-picoline instead of pyridine. Yield: 0.75 g (**3**); 0.73 g (**4**); and 0.72 g (**5**).

2.6. *Preparation of* $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(BB)]\cdot C_2H_5OH$ *(where BB = 1,10-phenanthroline (phen, 6); (2,2′-bipyridine) (bpy, 7))*

Complex **1** (1.00 g, 1.27 mmol) was suspended in ethanol (100 mL) accompanied by gentle stirring for 15 min at 60–70°C. A solution of 1,10-phenanthroline (0.76 g, 3.83 mmol) in ethanol (50 mL) for 1 : 3 molar ratio was added to this. The reaction mixture was refluxed for 3 h precipitating a light yellow compound. The compound was filtered hot, washed with hot ethanol and then with ether, and dried over anhydrous $CaCl_2$. Yield: 0.72 g.

Complex **7** was prepared in a similar manner using 2,2′-bipyridine instead of 1,10-phenanthroline. Yield: 0.71 g.

3. Results and discussion

The complexes isolated in the present study together with their molecular formula, color, decomposition point, percentage yield, analytical data, magnetic moment, molar conductance, and electronic spectral data are reported in table 1.

All of the complexes are colored, air stable and decompose above 300°C without melting, except **6** which melts at 217°C. Such thermal behavior of **6** indicates covalent character, whereas the remaining complexes are more ionic. All of the complexes are insoluble in water, partly soluble in ethanol, methanol, acetone, benzene, chloroform, hexane, and ether, and soluble in DMSO or DMF.

Efforts were taken to crystallize the complexes under different experimental conditions in DMSO and DMF. Thus, both saturated and dilute solutions of the complexes in various solvent systems such as DMSO, DMF, DMSO–CH_3CN, DMSO–CH_2Cl_2, DMF–CH_3CN, and DMF–CH_2Cl_2 were kept for 0.5, 1, and 2 months either at room temperature or under a freezer to grow crystals. Furthermore, the solutions were gently evaporated at 40°C, 50°C, and 60°C in a hot electronic oven to promote crystal growth. Efforts were also made to crystallize these complexes either by layering the above solutions with ether or by solvent diffusion methods. Unfortunately, in all our efforts only amorphous compounds precipitated, which prevented analyses of the complexes by X-ray crystallography.

All the complexes were diamagnetic indicating that molybdenum is +6 in these complexes with d^0 electronic configuration, indicating no reduction of the molybdenum(VI) under the influence of the ligand.

3.1. *Thermal studies*

The detailed decomposition studies [36] of **1**, **2**, **4**, and **5** were carried out in the temperature range of 60–250°C. The weight loss occurs in two prominent steps, i.e., 75–80°C and 200–240°C, for **2**, **4**, and **5** while **1** showed weight loss in the range of 70–80°C and 160–180°C. The vapors evolved in the range of 75–80°C in all of the complexes gave a yellow precipitate with a solution of sodium hydroxide and iodine, confirming that they are ethanol. The loss of ethanol molecules in the temperature range of 75–80°C indicates that they are present in the lattice of the complexes. Weight loss corresponds to one ethanol supporting the number of ethanol molecules present. When vapors in the range of 160–180°C in **1** were passed over anhydrous copper sulfate in a test tube, it turned blue, confirming the presence of water. The loss of weight corresponds to two water molecules in the coordination sphere of the metal [36]. Complexes **2**, **4**, and **5** showed further weight loss in the range of 200–240°C. The vapors evolved from **2** in this temperature range turned the color of $CHCl_3$ containing a drop of 5 M NaOH solution to red, confirming the presence of pyridine. Similarly, vapors evolved from **4** and **5** in this temperature range turned the color of cyanogen bromide solution to green-violet and blue, respectively, on treatment with phloroglucinol solution, suggesting the presence of 3-picoline and 4-picoline in **4** and **5**, respectively. The weight loss in this temperature range corresponds to one molecule each of pyridine, 3-picoline, and 4-picoline per metal center.

Table 1. Analytical data and physical properties of homobimetallic Mo(VI) complexes derived from H_4nsh.

Sl. no.	Ligand/Complex and color	D.P. (°C)	Yield (%)	Anal.: Found (Calcd) (%) Mo	C	H	N	Molar conductance (Λ_M) $Ohm^{-1} cm^2 mol^{-1}$	Electronic spectral bands λ_{max} (nm) (ε_{max} $dm^3 mol^{-1} cm^{-1}$)
	H_4nsh	254	72	–	69.19 (68.72)	4.82 (4.84)	12.65 (12.33)	–	311 (4460), 323 (650), 355 (5280), 371 (5560)
1	$[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ Orange $Mo_2C_{28}H_{28}O_{11}N_4$	>300	75	24.55 (24.34)	42.44 (42.66)	3.53 (3.58)	6.92 (7.11)	4.29	303 (12,842), 321 (16,785), 353 (13,952), 368 (12,804), 429 (1014)
2	$[(MoO_2)_2(nsh)(py)_2]\cdot C_2H_5OH$ Orange $Mo_2C_{38}H_{33}O_9N_6$	>300	66	20.80 (21.20)	50.42 (50.18)	3.72 (3.66)	9.56 (9.24)	3.31	309 (14,034), 321 (18,013), 354 (15,618), 368 (14,430), 436 (1663)
3	$[(MoO_2)_2(nsh)(2\text{-pic})_2]\cdot C_2H_5OH$ Orange $Mo_2C_{40}H_{38}O_9N_6$	>300	71	20.75 (20.44)	52.12 (51.88)	4.14 (4.08)	8.78 (8.95)	2.92	303 (12,487), 321 (16,370), 354 (13,728), 368 (12,608), 431 (920)
4	$[(MoO_2)_2(nsh)(3\text{-pic})_2]\cdot C_2H_5OH$ Orange $Mo_2C_{40}H_{38}O_9N_6$	>300	66	20.76 (20.44)	52.06 (51.88)	4.12 (4.08)	8.81 (8.95)	3.13	308 (14,108), 321 (18,231), 354 (15,069), 368 (13,888), 433 (1500)
5	$[(MoO_2)_2(nsh)(4\text{-pic})_2]\cdot C_2H_5OH$ Orange $Mo_2C_{40}H_{38}O_9N_6$	>300	65	20.66 (20.44)	51.98 (51.88)	4.02 (4.08)	8.82 (8.95)	4.53	308 (15,729), 322 (19,932), 354 (17,230), 368 (15,870), 433 (1981)
6	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(phen)]\cdot C_2H_5OH$ Light yellow $Mo_2C_{40}H_{36}O_{11}N_6$	217	62	20.11 (19.80)	49.88 (49.58)	3.79 (3.74)	8.87 (8.71)	2.81	308 (15,826), 321 (19,948), 355 (19,428), 368 (18,287), 430 (1180)
7	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(bpy)]\cdot C_2H_5OH$ Pale yellow $Mo_2C_{38}H_{36}O_{11}N_6$	>300	61	20.52 (20.30)	48.63 (48.30)	3.88 (3.84)	8.97 (8.94)	2.29	308 (16,918), 321 (21,466), 353 (18,282), 368 (15,423), 432 (2036)

3.2. *Molar conductance*

All of the complexes have molar conductance values from 1.2 to 4.7 $cm^2 Ohm^{-1} mol^{-1}$ in DMSO at 10^{-3} M, suggesting that they are nonelectrolytes [37].

3.3. *Electronic spectra*

Electronic spectra of the complexes have been recorded in DMF at 10^{-3} M. The ligand shows bands at 310–325 nm and 350–370 nm assigned to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. These blue bands shift on complexation. This indicates that dihydrazone is coordinated to the metal. In addition to the intraligand bands, all of the complexes show a new band at 429–436 nm, assigned to ligand-to-metal charge transfer (LMCT).

3.4. *^{1}H NMR spectra*

The two proton doublets (Supplementary material) are observed at δ 11.61 and 12.73 ppm and two proton singlets at δ 9.99 and 11.14 ppm in the ^{1}H NMR spectra of the free dihydrazone. These signals are assigned to naphtholic –OH and secondary NH, respectively. These signals do not appear in the ^{1}H NMR spectra of **1**–**5**. The absence of signals in the region δ 20–11 ppm in the complexes indicates the coordination of dihydrazone in the enol form through naphtholic oxygen via deprotonation and carbonyl oxygen via enolization/deprotonation. The ligand shows doublets at δ 9.05 and δ 8.60 ppm assigned to azomethine protons which shift downfield about 0.32–0.52 ppm in **1**–**5**. The downfield shift is attributed to the loss of electron density from the nitrogen of azomethine group to the metal [33]. The most crucial feature of the ^{1}H NMR spectra of **1**–**5** is the collapse of the doublets corresponding to δ-CH=N in the free ligand into a single resonance, suggesting that the dihydrazone which exists in the *anti*–*cis* configuration in the free state attains *staggered* configuration in **1**–**5**. Similar coordination of the related malonoyl dihydrazone to the metal has been reported by Gopinath *et al.* [31] and Lal *et al.* [38]. The naphthyl proton multiplet appears at δ 7.15–8.23 ppm in **1**–**5**; **2**–**5** show additional resonances in the region δ 7.16–8.57 ppm from *ortho* proton(s) of pyridine, 2-picoline, 3-picoline, and 4-picoline. These signals are upfield shifted compared to their position in free pyridine, 2-picoline, 3-picoline, and 4-picoline [36], attributed to the coordination of pyridyl nitrogen. The methyl proton signals also show upfield shift in the complexes compared to their position in free picoline, indicating the coordination of ring nitrogen.

The ^{1}H NMR spectra of **6** and **7** are significantly different compared to **1**–**5**. The two proton doublets at δ 11.61 and δ 12.73 ppm due to naphtholic –OH protons in the free dihydrazone are upfield shifted in **6** and **7** to δ 11.60–12.59 ppm. Similarly, δ NH protons at δ 9.99 and 11.14 ppm are downfield shifted to δ 11.14 in both the complexes. The presence of δ NH in these complexes suggests that the dihydrazone is coordinated in the keto form. The azomethine proton signals, on average, show a downfield shift by about δ 0.32–0.21 ppm as a doublet in these complexes as against a singlet in **1**–**5**. Such a feature associated with δ (–CH=N) may be attributed to coordination of the dihydrazone to the metal center in the *anti*–*cis* configuration [39] in which only the azomethine nitrogens of the dihydrazone are coordinated to the metal. As a result of *anti*–*cis* configuration of the ligand, one hydrazone attains axial position while the other remains equatorial. Hence, equatorial protons appear upfield as compared to axial protons and coupling between axial protons and equatorial protons leads to a doublet for each. Stereospecific long-range coupling has been reported in hydrazones [39, 40]. The naphthyl proton multiplet appears in the region of δ 7.15–8.23 ppm in these complexes, merged with signals due to aromatic protons of 1,10-phenanthroline and 2,2′-bipyridine. All the complexes show a triplet, a quartet, and a triplet at δ 1.04, δ 3.44–3.01, and δ 4.36–4.34 ppm, respectively, which correspond to methyl, methylene, and –OH of ethanol present in the lattice.

3.5. *^{13}C nuclear magnetic resonance spectroscopy*

Complexes **1**, **3**, and **5** were characterized by ^{13}C NMR spectroscopy (Supplementary material). Comparison of the ^{13}C NMR spectra of the ligand and the complexes indicates that the ligand and complexes have different configuration. Hence, the spectral features of the complexes (with respect to the number of signals) are entirely different from that of the ligand. The ^{13}C NMR spectra of the free ligand and **3** are provided in Supplementary material.

Signals associated with carbons near the coordinated sites in the complexes are remarkably deshielded in comparison to the free ligand. The effect of molybdenum on carbon resonances of naphthyl ring thus shifts upfield the signals due to C(6), C(7), C(8), and C(9) by 1.46–2.44 ppm, while those due to C(3a), C(11), and C(13) are shifted upfield even more since they are closer to the coordinated oxygen and nitrogen. As a consequence, signals due to C(2a) and C(2b), which are in the free ligand were at δ 195.32 and 187.24 ppm, respectively, appear at δ 172.26 ppm. The signal at δ 160.00 ppm assigned to C(13) in the free ligand was observed at δ 167.48 and 167.22 ppm giving a chemical shift change of 7.35 ppm. Similarly, the signal at δ 151.61 ppm is assigned to azomethine carbon which in the free ligand was at 160.81 and 159.86 ppm giving a chemical shift change of 8.73 ppm. The signals at δ 132.41 and 124.65 ppm are assigned to C(10) and C(5) which in the free dihydrazone were at δ 134.47 and 132.20 ppm and δ 127.63 and 127.43 ppm giving chemical shift changes of 0.93 and 2.88 ppm, respectively. The signal at δ 108.35 ppm assigned to C(4) in the free ligand remained almost unaltered.

^{13}C NMR spectrum of the ligand shows 13 resonances and all of the signals appear as pairs except signals due to C(12), C(4), and C(7). Each resonance forms a pair which corresponds to the axial and equatorial carbon atoms. ^{13}C NMR spectra of the complexes shows 13 signals only, all as a singlet, supporting staggered configuration of the ligand coordinated, which are consistent with ^{1}H NMR spectra.

3.6. *Infrared spectra*

A comparison of the IR spectra of the complexes with that of the free ligand H_4nsh (Supplementary material) suggests that the dihydrazone coordinates to the metal center in enol form in all complexes except **4** and **7** in which the ligand coordinates in keto form.

The IR spectra of **1**–**5** are drastically changed compared to the free dihydrazone. The strong band at 1672 cm^{-1} assigned to ν(C=O) of the uncoordinated dihydrazone disappears in the complexes, again suggesting the collapse of the amide structure of the ligand in coordination to the metal through carbonyl oxygen in the enol form [31]. In the free dihydrazone, ν(C=N) appears as a couple of bands at 1633 and 1593 cm^{-1}, shifting to 1623–1602 cm^{-1} in **1**–**5**, indicating the coordination of azomethine nitrogen.

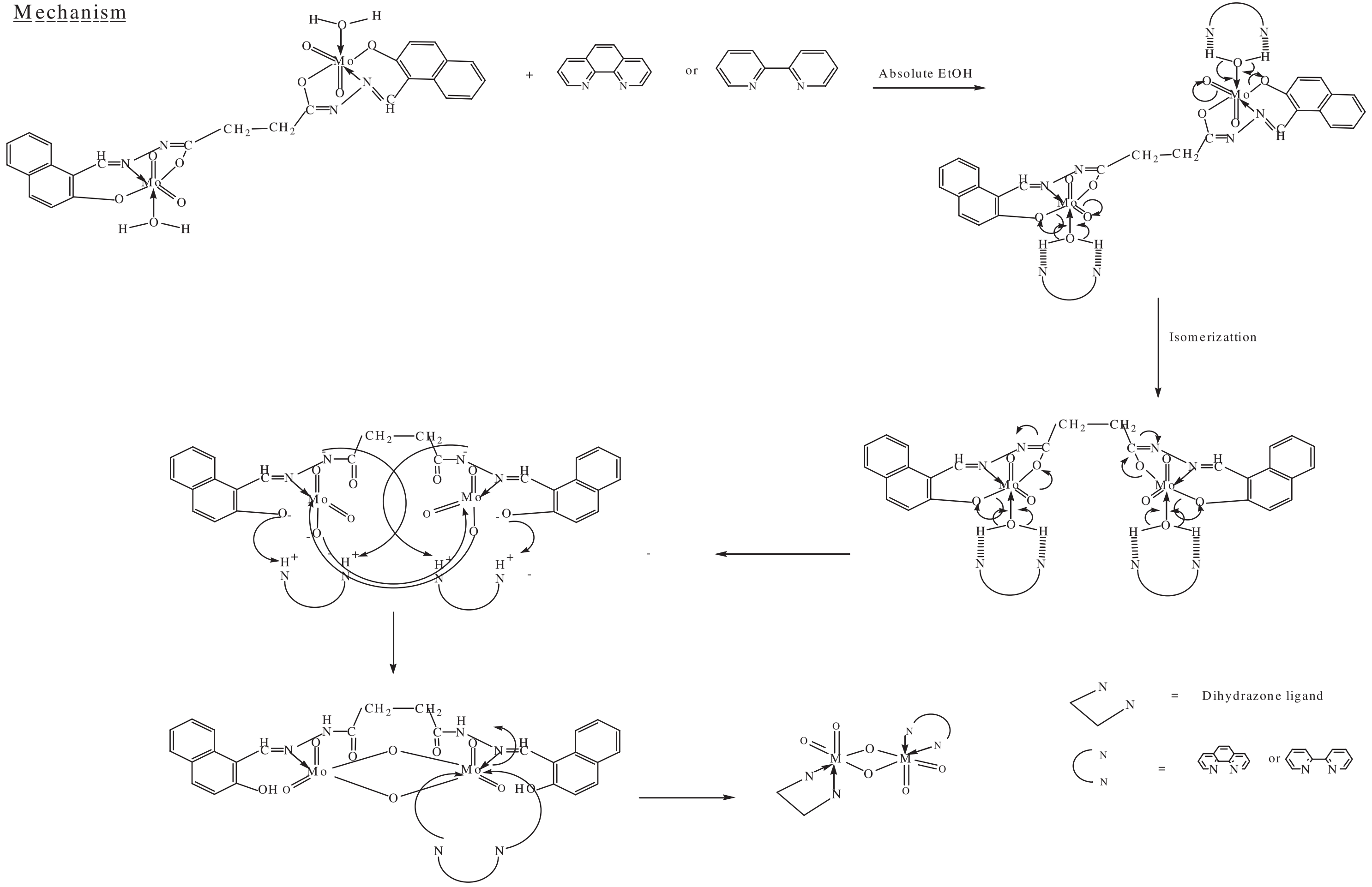
The free dihydrazone shows a medium intensity band at 1540 cm^{-1} due to mixed contribution of amide II and ν(C–O) (naphtholic) [36]. This band shows a considerable shift to higher frequency in **1**–**5**, 1554–1558 cm^{-1}. Such a shift indicates bonding through naphtholic oxygen via deprotonation [36]. The intensity of the band in this region is considerably increased compared to that in free dihydrazone, probably due to overlap with the band due to newly created NCO^- as a result of enolization [29]. Complexes **2**–**5** show a new, but very weak, band in the region 1036–1065 cm^{-1} characteristic of coordinated pyridine, 2-picoline, 3-picoline, and 4-picoline.

IR spectra of **6** and **7** are very similar to the uncoordinated dihydrazone, indicating secondary NH and naphtholic –OH in the complexes. The strong amide I band at 1672 cm^{-1} in the free ligand shifts to 1675 cm^{-1}, suggesting nonbonding of $>C=O$ [27]. A couple of strong bands at 1633 and 1503 cm^{-1} assigned to ν(C=N) shift to lower frequency by 2–3 cm^{-1}, indicating the coordination of azomethine nitrogen to the metal. The medium intensity band at 1540 cm^{-1} due to the mixed contribution of amide II and ν(C–O) (naphtholic) remains almost unshifted in **6** and **7**, indicating noninvolvement of $>C=O$ and naphtholic –OH in coordination.

Intense bands at 636 and 725 cm^{-1} due to out-of-plane motion of the hydrogen on the heterocyclic ring and the central ring [41] were observed in the IR spectrum of **6**. Comparison with the bands at 787 and 734 cm^{-1} in the IR spectrum of free 1,10-phenanthroline indicates that these bands shift to lower frequency upon complexation. Characteristic bands of free bipyridine [42] due to C–H out-of-plane deformation as a strong band at 758 cm^{-1} and a weak satellite at 739 cm^{-1} are shown in **7**. The band at 758 cm^{-1} was almost unshifted, while the weak satellite at 739 cm^{-1} shifts to 622 cm^{-1}. The presence of these bands in **6** and **7** indicate the bidentate N–N coordination of 1,10-phenanthroline and 2,2′-bipyridine [41, 42]. All complexes show two very strong to medium intensity bands in the region 884–956 cm^{-1}, indicating *cis*-MoO_2^{2+}. The ν(Mo=O) of **6** and **7** shift considerably to lower frequency compared to those in corresponding pyridine and substituted pyridine analogues. The band of medium intensity at 780–796 cm^{-1} in **6** and **7** is assigned to the stretching of doubly bridged Mo_2O_2.

From the stoichiometry of **6** and **7** and spectral evidence presented above, an additional oxo-group was generated during the reaction of **1** with 1,10-phenanthroline and 2,2′-bipyridine, but not for **2**–**5**. Hence, bidentate ligands induce the migration of protons from water coordinated to molybdenum, generating an oxo-group which binds to molybdenum center in **6** and **7**; monodentate nitrogen donors are unable to induce migration of protons from water. The probable mechanism for the generation of the oxo groups in **6** and **7** is shown in scheme 1. Phenanthroline and bipyridine are able to simultaneously bind the two hydrogens of water, breaking the O–H bond and generating an oxo. Once the bidentate ligands are hydrogen bonded to water, the complex undergoes isomerization to *anti–cis* configuration where MoO_2^{2+} groups are brought closer to each other.

Mechanism



Scheme 1. Mechanism showing the generation of oxo-group from water coordinated to MoO_2^{2+}.

4. Conclusion

Some transition metal complexes of monoacyl-, aroyl-, and pyridoyl-hydrazones have appeared, yet those derived from multihydrazines have received attention in recent years only. All of the studies reported so far describe the first series transition metal complexes of monohydrazones and multihydrazones, those on the second transition series metal complexes are virtually absent. In this article, some homobimetallic complexes of molybdenum from polyfunctional H_4nsh have been reported. The reaction of the dihydrazone H_4nsh with $MoO_2(acac)_2$ in 1 : 3 molar ratio yields homobimetallic molybdenum(VI) complex (**1**). Reaction with excess pyridine and substituted pyridines yield **2**–**5**. The dihydrazone coordinates to the metal as a tetrabasic hexadentate ligand in enol form and assumes staggered configuration in **1**–**5**. The ^{1}H NMR spectra suggest that the dihydrazone, which exists in *anti–cis* configuration uncoordinated, isomerizes to staggered configuration in the metal complexes. In *staggered* configuration, the different hydrazone parts of the dihydrazone are coordinated to different metal centers through naphtholate and enolate oxygens and azomethine nitrogens. In **6** and **7**, the dihydrazone is coordinated to the metal center as a neutral bidentate ligand in the keto form through azomethine nitrogens only in *anti–cis* configuration. The bidentate 1,10-phenanthroline and bipyridine ligands induce

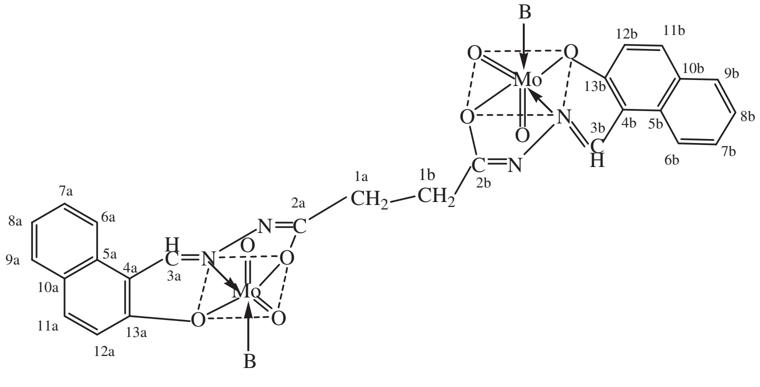
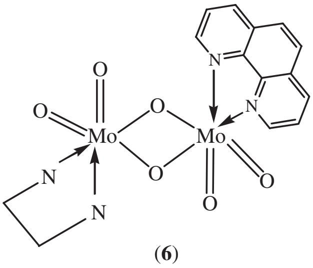
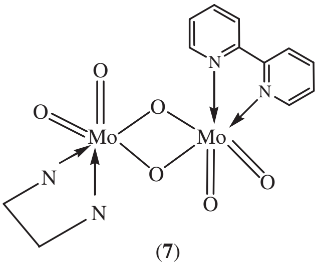


Figure 2. Structure along with numbering scheme of the carbon atoms in $[(MoO_2)_2(nsh)(B)_2]\cdot C_2H_5OH$ (B = H_2O (**1**), py (**2**), 2-pic (**3**), 3-pic (**4**), 4-pic (**5**)).



(**6**)



(**7**)

Figure 3. Tentative structure of $[(\mu_2\text{-}O)(MoO_2)_2(H_4nsh)(BB)]\cdot C_2H_5OH$ (BB = 1,10-phenanthroline (**6**), 2,2′-bipyridine (**7**)).

transfer of oxygen from coordinated water molecules to molybdenum. To the best of our knowledge, this is the first work in hydrazone coordination chemistry in which the transfer of oxygen from coordinated water to the ligated metal has been reported.

On the basis of various physico-chemical and spectral studies and their discussion as given above, the complexes are suggested to have the structures shown in figures 2 and 3.

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