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Synthesis and characterization of Mo(VI) complexes derived from ONO donor acylhydrazones

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ABSTRACT

Four new dioxomolybdenum(VI) complexes were prepared using different acylhydrazones. Hydrazones used for complexation were derived from 2-hydroxy-4-methoxybenzaldehyde, 2-hydroxy-4-methoxyacetophenone, benzhydrazide and nicotinoyl hydrazide. The complexes were characterized by various spectroscopic techniques, thermal and elemental analyses. The ^{1}H NMR and IR spectral data indicate tridentate nature of the ligands through enolization. IR spectra provide information about the dimeric nature of the complexes. The thermal analyses of the complexes showed the presence of lattice water in some of the complexes.

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1. Introduction

Recently molybdenum chemistry has gained considerable attention due to versatile applications of molybdenum and its complexes in the fields of catalysis and biology [1,2]. Among the second series of transition metals, molybdenum is the only biometal important for living kingdom with a large number of stable and accessible oxidation states. The importance of molybdenum as a biological trace element depends on its contribution in various molybdoenzymes. The dioxomolybdenum complexes have been widely studied, as models for the active sites of oxotransfer molybdoenzymes like sulfite and aldehyde oxidase, xanthine oxidase, xanthine dehydrogenase and nitrate reductase [3–5]. In the catalytic activity of molybdoenzymes, the oxidation state of molybdenum varies between VI and IV states and Mo(V) coexists with Mo(VI) and Mo(IV) [6]. The presence of cis-MoO_2^{2+} group in the oxidized form of some molybdoenzymes stimulate the search for new compounds in which this moiety is coordinated to ligands containing heteroatoms like O, N and S. The cofactors of these enzymes are most probably coordinatively unsaturated and this helps the easy binding of substrate. The study of molybdenum complexes with dianionic tridentate ligands is particularly significant because the coordination of cis-MoO_2^{2+} with dianionic tridentate ligand systems provides an open active site on molybdenum [7]. The catalytic activities of dioxomolybdenum complexes were proved by several reports [8,9]. There are many reports regarding the studies of dioxomolybdenum complexes with O, N and S containing ligands [10–12]. Ligands with heteroatom in their structure act as good chelating agents for complex formation. The intensified interests in the study of metal complexes with hydrazones are consequences of their increasing applications in different areas like medicinal, biological, industrial and analytical chemistry [13–15]. Our interest behind the study of molybdenum complexes with hydrazones lies in the fact that the information gained during the study of these complexes may be useful to reveal the enzyme structures and their functions which are not readily obtained by studying the enzymes themselves. As an extension of our work on the syntheses and characterization of transition metal complexes with hydrazones [16,17], here we report the syntheses and spectral perspectives of four dioxomolybdenum complexes with different ONO donor hydrazones.

2. Experimental

2.1. Materials

2-Hydroxy-4-methoxyacetophenone (Aldrich), 2-hydroxy-4-methoxybenzaldehyde (Aldrich), nicotinic acid hydrazide (Aldrich), benzhydrazide (Aldrich) and $MoO_2(acac)_2$ (Aldrich) were used without further purification. Solvent used was methanol.

2.2. Synthesis

2.2.1. Syntheses of acylhydrazones

The syntheses of 2-hydroxy-4-methoxybenzaldehyde nicotinoylhydrazone monohydrate ($H_2hmbn{\cdot}H_2O$) and 2-hydroxy-

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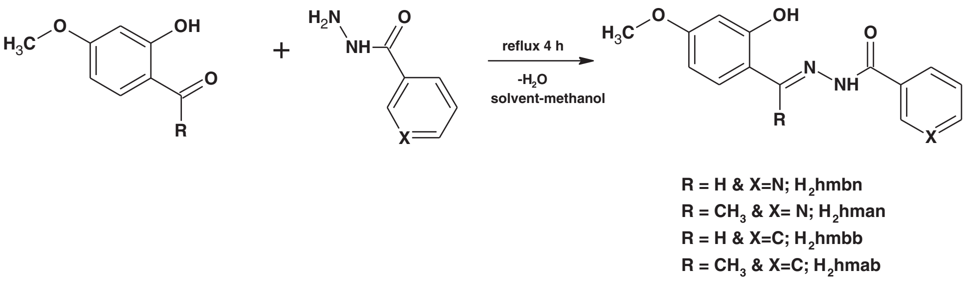


Scheme 1. Syntheses of hydrazones.

4-methoxyacetophenone nicotinoylhydrazone (H_2hman) have been reported by us earlier [16,17]. 2-Hydroxy-4-methoxybenzaldehyde benzoylhydrazone (H_2hmbb) and 2-hydroxy-4-methoxyacetophenone benzoylhydrazone (H_2hmab) were synthesized by refluxing an equimolar mixture of the benzhydrazide and corresponding aldehyde/ketone in the presence of 1–2 drops of glacial acetic acid in methanol for 4 h. Scheme 1 describes the syntheses of acylhydrazones.

Elemental Anal. Found (Calcd.) (%):
H_2hmbb: C, 66.08 (66.66); H, 5.47 (5.22); N, 10.26 (10.36).
H_2hmab: C, 67.25 (67.59); H, 5.61 (5.67); N, 9.68 (9.85).

2.2.2. *Syntheses of complexes*

The complexes [MoO_2hmbn]$_2\cdot H_2O$ (**1**), [MoO_2hman]$_2\cdot H_2O$ (**2**), [MoO_2hmbb]$_2\cdot H_2O$ (**3**) and [MoO_2hmab]$_2$ (**4**) were prepared in a similar way by refluxing methanolic solutions of $MoO_2(acac)_2$ (1 mmol, 0.326 g) with H_2hmbn$\cdot H_2O$ (1 mmol, 0.289 g), H_2hman (1 mmol, 0.285 g), H_2hmbb (1 mmol, 0.270 g) and H_2hmab (1 mmol, 0.284 g) respectively. Initially on mixing, the solutions turn to an orange color and after refluxing for 4 h the complexes separated. All the four complexes are orange colored. Our attempts to get single crystals suitable for X-ray diffraction studies were not successful. Scheme 2 illustrates the syntheses of complexes and the water molecules are omitted in the scheme.

Elemental Anal. Found (Calcd.) (%):
[MoO_2hmbn]$_2\cdot H_2O$ (**1**): C, 41.50 (41.40); H, 2.29 (2.98); N, 10.57 (10.34).
[MoO_2hman]$_2\cdot H_2O$ (**2**): C, 42.85 (42.87); H, 3.20 (3.36); N, 10.17 (10.00).
[MoO_2hmbb]$_2\cdot H_2O$ (**3**): C, 44.87 (44.46); H, 3.64 (3.23); N, 6.57 (6.91).
[MoO_2hmab]$_2$ (**4**): C, 46.14 (46.84); H, 3.32 (3.44); N, 6.86 (6.83).

2.3. *Physical measurements*

Elemental analyses of the acylhydrazones and their molybdenum complexes were carried out using a Vario EL III CHNS analyzer at SAIF, Kochi, India. Infrared spectra were recorded on a JASCO FT/IR-4100 type A spectrometer in the range 4000–400 cm^{-1} using KBr pellets. Electronic spectra were recorded on a Cary 5000 version 1.09 UV–VIS–NIR spectrophotometer using acetonitrile as the solvent. NMR spectra of the complexes and ligands were recorded in DMSO solutions in a Bruker AMX 400 FT-NMR Spectrometer using TMS as the internal standard at the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, India. Magnetic susceptibility studies were done with Gouy balance. TG–DTG analyses of the prepared complexes were carried out on a Perkin Elmer, Diamond thermogravimetric analyzer. The heat flow used was 10 °C/min under nitrogen atmosphere over a temperature range of 50–1000 °C. The molar conductivities were determined for all the four complexes in 10^{-3} M DMF solutions. The electrochemical behavior of the complexes and free hydrazones was studied in DMF solutions by cyclic voltammetry on a CHI 608D electrochemical analyzer with platinum disc as working electrode. The counter electrode used was platinum wire and Ag/Ag^+ the reference electrode. The supporting electrolyte used was tetrabutylammonium phosphate (TBAP).

3. Results and discussion

All the four complexes were synthesized in an identical way and in all of them hydrazones act as tridentate dianionic ONO donor ligands towards MoO_2^{2+} centre. The experimental and calculated analytical data are in very close agreement. Magnetic susceptibility studies indicate diamagnetic nature of these complexes and from this it is evident that Mo is in +6 oxidation state. The cyclic voltammograms of the complexes did not show any redox properties. Reversible one electron reduction of $[MoO_2]^{2+}$ complexes to analogous $[MoO_2]^+$ complexes is uncommon and occurs only when aprotic ligands and solvents are used and when the ligand has sufficient steric bulk to prevent dimerization [18]. So the absence of redox behavior is an evidence for the dimeric nature of the compounds.

3.1. *Conductance measurements*

The molar conductivity values for all the four complexes in 10^{-3} M DMF solutions are in the range of 2–5 $ohm^{-1}\,cm^2\,mol^{-1}$ which is much less than the value of 65–90 $ohm^{-1}\,cm^2\,mol^{-1}$ reported for a 1:1 electrolyte in the same solvent [19]. So the conductance measurements in DMF suggest that they are non-electrolytes.

3.2. *Thermal studies*

The thermal analyses give information concerning the thermal stability and nature of water molecules in complexes. Reports show that the weight losses for lattice water are in the range of 50–130 °C [20,21]. The complexes 1, 2 and 3 showed loss of weight which corresponds to one water molecule in the temperature range 80–110 °C indicate the presence of lattice water in these complexes. In complex 4, there was no weight loss in the region below 250 °C which shows the absence of water molecule. All the complexes showed weight losses in the temperature range 250–750 °C due to the decomposition of ligands. Above 750 °C a plateau is observed which corresponds to the formation of MoO_3. TG–DTG curves of complexes 1 and 4 are shown in Figs. 1 and 2.

3.3. *Infrared and electronic spectral studies*

The most interesting vibrational frequencies of acylhydrazones and their molybdenum complexes, which help us to understand the coordination environment of the metal in these complexes, are given in Table 1. In the IR spectra of the free hydrazones, bands due

Table 1
Selected IR bands (cm^{-1}) with tentative assignments of Mo(VI) complexes.

Compound	ν(C=O)	ν(C=N)	ν(N=C)	ν(N–N)	ν(C–O)	ν(Mo=O)	ν(Mo=O–Mo)
$H_2hmbn \cdot H_2O$	1643	1604	–	1110	1284	–	
$[MoO_2hmbn]_2 \cdot H_2O$ (**1**)	–	1589	1540	1129	1225	903, 937	833
H_2hman	1638	1602	–	1135	1262	–	
$[MoO_2hman]_2 \cdot H_2O$ (**2**)	–	1593	1532	1140	1249	913, 942	854
H_2hmbb	1630	1600	–	1130	1286	–	
$[MoO_2hmbb]_2 \cdot H_2O$ (**3**)	–	1596	1535	1138	1230	910, 930	850
H_2hmab	1650	1601	–	1127	1265	–	
$[MoO_2hmab]_2$ (**4**)	–	1597	1549	1156	1234	913, 942	854

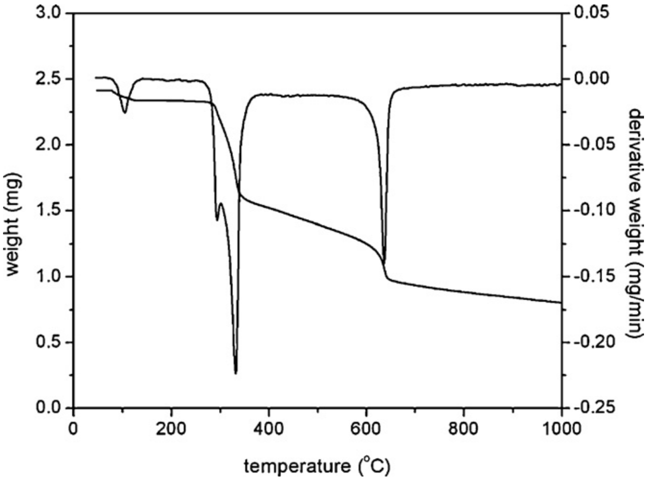


Fig. 1. TG–DTG plot of $[MoO_2hmbn]_2 \cdot H_2O$ (**1**).

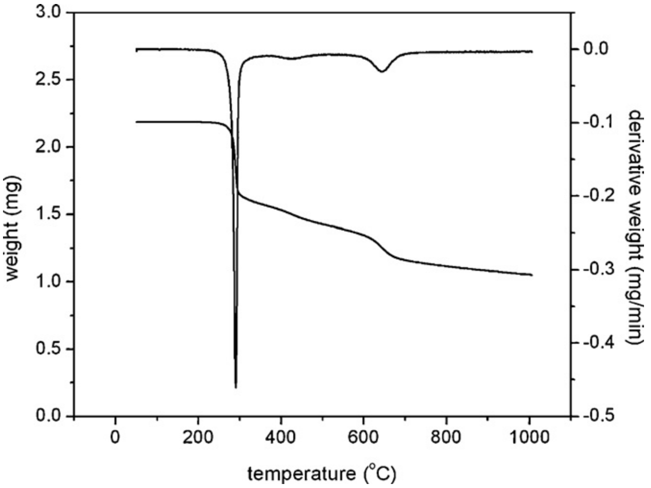
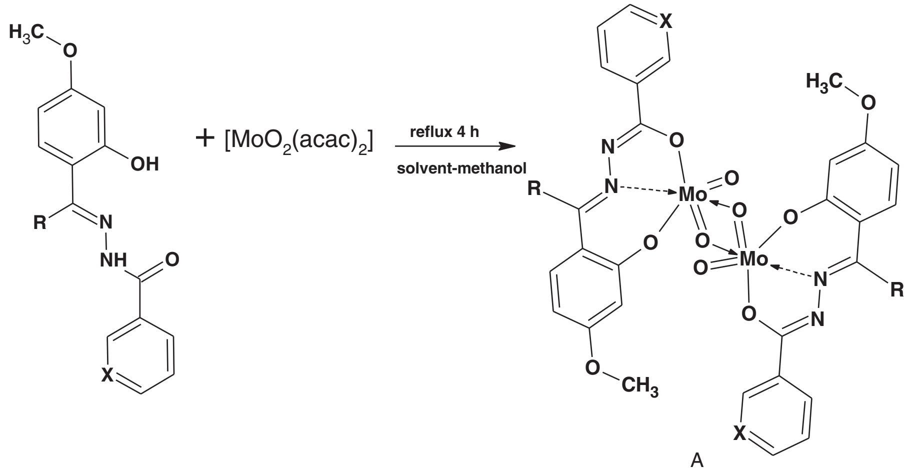


Fig. 2. TG–DTG plot of $[MoO_2hmab]_2$ (**4**).

to carbonyl group are observed in the region 1630–1650 cm^{-1} and these are absent in the spectra of the complexes which suggests enolization of ligands. This is also confirmed from the fact that the O–H and N–H stretching frequencies observed around 3220 and 3035 cm^{-1} in free hydrazones were found to be absent in complexes. Another result obtained from this is that the ligands are coordinated in a dianionic form in these complexes.

IR spectra of all compounds except **4** showed broad bands around 3430 cm^{-1} which indicate the presence of lattice water. The azomethine bands of the acylhydrazones found in the range 1600–1605 cm^{-1} are shifted to lower frequencies by 4–15 cm^{-1} in the spectra of the complexes, indicating the coordination of azomethine nitrogen to the metal [22]. The increase in ν(N–N) bands in complexes, due to the increase in double bond character confirm the coordination of the ligands through the azomethine nitrogen [23]. The ν(C–O) bands present in ligands are shifted to lower frequencies in complexes suggesting the coordination of the phenolic oxygen. In all complexes two bands are observed in the



R = H & X=N; A = Complex 1
R = CH_3 & X= N; A = Complex 2
R = H & X=C; A = Complex 3
R = CH_3 & X=C; A= Complex 4

Scheme 2. Syntheses of complexes.

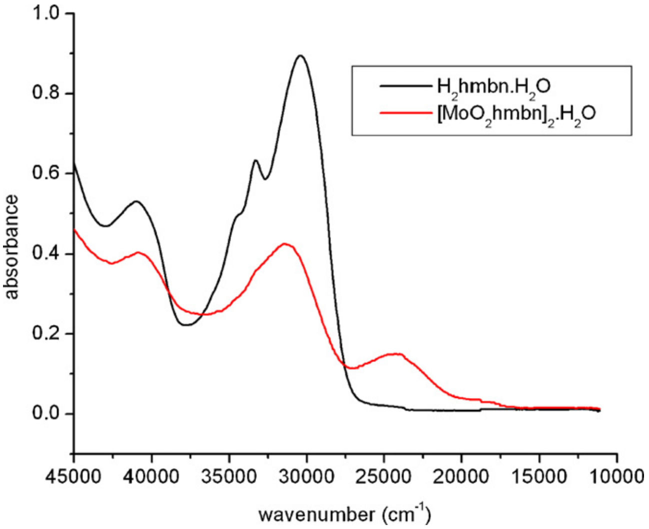


Fig. 3. Electronic spectra of $H_2hmbn{\cdot}H_2O$ and $[MoO_2hmbn]_2{\cdot}H_2O$.

region 900–950 cm^{-1} which can be assigned to symmetric and antisymmetric vibrations of the *cis*-MoO_2^{2+} core [24]. As per previous reports structurally characterized dimeric dioxomolybdenum(VI) complexes of tridentate ligands have sharp bands in the region 800–850 cm^{-1} [25,26]. Here the presence of a band in the above said region indicates the formation of dimeric dioxomolybdenum complexes.

The electronic spectra of all the four acylhydrazones showed bands in the region 30,500–42,000 cm^{-1} due to π–π^* transitions. The n–π^* transitions that are forbidden by the selection rules are not observed in these compounds. In the electronic spectra of complexes these transitions are slightly shifted. Fig. 3 illustrates the shift in transitions of one of the ligands, $H_2hmbn{\cdot}H_2O$ on complexation. The complexes show strong bands ~24,400 cm^{-1} and are assigned as ligand to metal charge transfer transitions [25–27]. Electronic spectra of the complexes are presented in Fig. 4 and the assignments are listed in Table 2.

3.4. NMR spectral studies

Proton Nuclear Magnetic Resonance (^{1}H NMR) Spectroscopy is a powerful tool used for the determination of the structure of compounds. Because of their diamagnetic nature, the complexes were studied by NMR spectroscopy. The ^{1}H NMR spectra of the ligands and complexes have been recorded with DMSO as solvent. In the spectra of the free hydrazones there are sharp singlets in the region 12–14 ppm with an area integral of one which is due to phenolic OH protons. They also gave singlets in the range 11–12 ppm due to another proton showing the existence of iminol form in solution. Large δ values of these protons may be due to intramolecular hydrogen bonding. Upon D_2O exchange, the intensity of these signals significantly decreases, which suggests that these protons are easily exchangeable and confirm the assignment. The singlets with an area integral of three in the range of 3–3.8 ppm indicate the presence of three methoxy hydrogens. Peaks for aromatic protons were found in the region 6–8 ppm. Peaks corresponding to OH and NH protons were absent in the spectra of complexes and this is a clear cut evidence for the coordination of ligands in the enolic form, *i.e.* from NMR spectra, the coordination of ligands in the dianionic form is confirmed. The peaks corresponding to the aromatic pro-

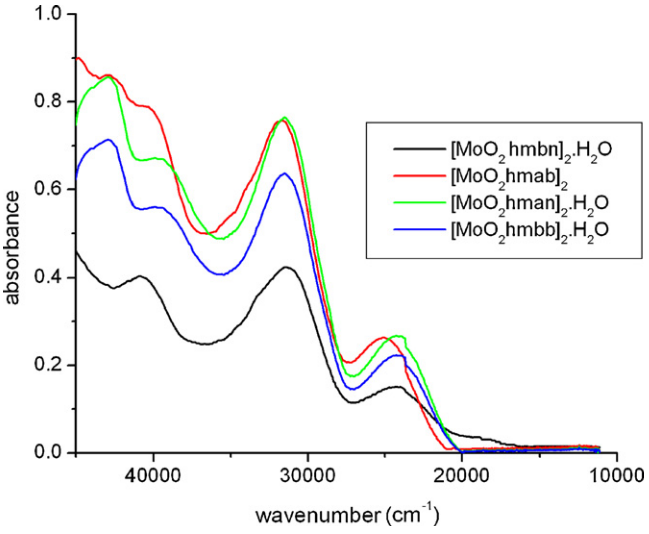


Fig. 4. Electronic spectra of the complexes.

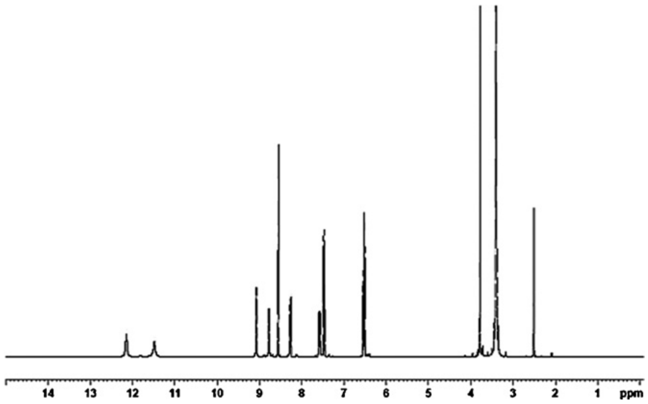


Fig. 5. ^{1}H NMR spectrum of $H_2hmbn{\cdot}H_2O$.

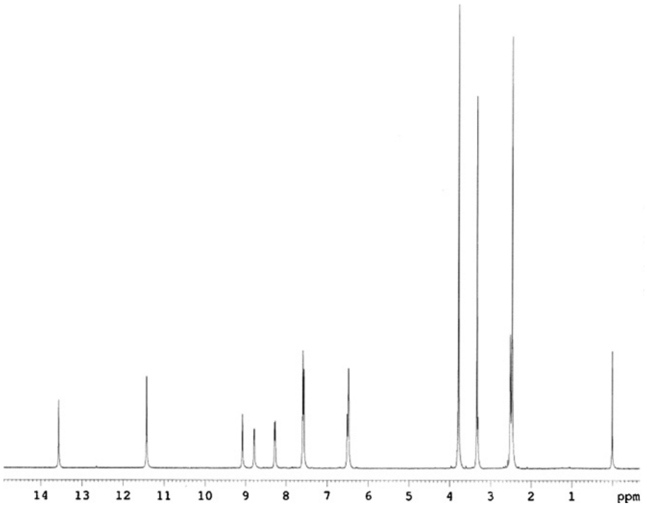


Fig. 6. ^{1}H NMR spectrum of H_2hman.

Table 2
Electronic spectral assignments (cm^{-1}) of Mo(VI) complexes.

Compound	Intraligand transitions	Charge transfer transition
$[MoO_2hmbn]_2{\cdot}H_2O$ (**1**)	31,360, 40,910	24,230
$[MoO_2hman]_2{\cdot}H_2O$ (**2**)	31,580, 39,600, 42,840	24,150
$[MoO_2hmbb]_2{\cdot}H_2O$ (**3**)	31,640, 39,740, 42,830	24,230
$[MoO_2hmab]_2$ (**4**)	31,640, 40,360, 42,550	24,970

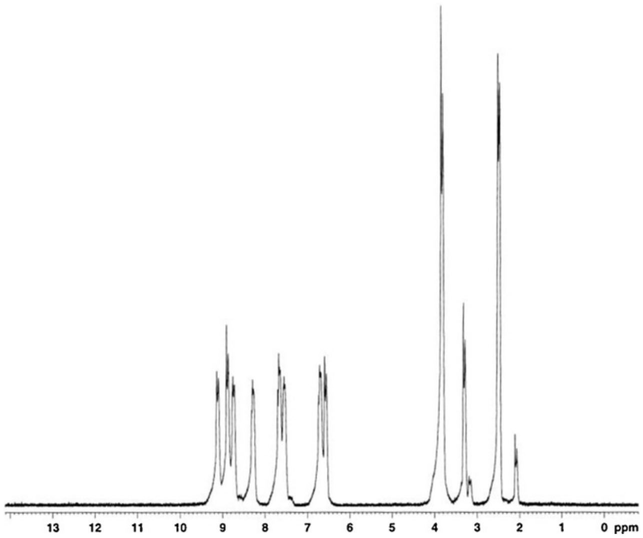


Fig. 7. ^{1}H NMR spectrum of $[MoO_2hmbn]_2{\cdot}H_2O$.

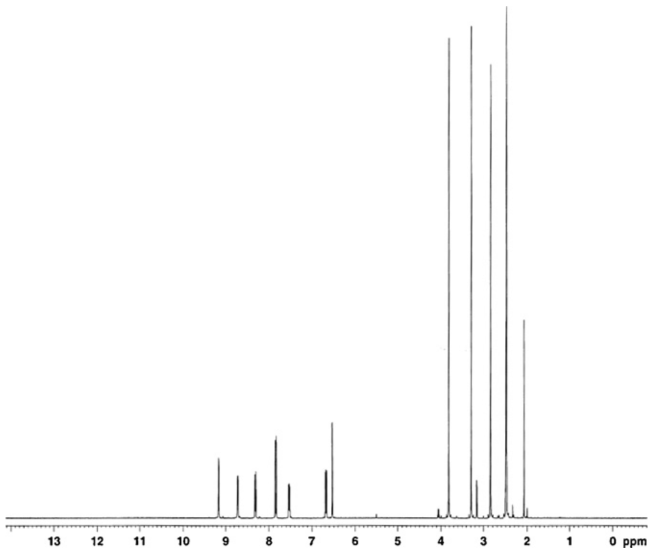


Fig. 8. ^{1}H NMR spectrum of $[MoO_2hman]_2{\cdot}H_2O$.

tons do not show much shift in complexes. The ^{1}H NMR spectra of H_2hmbn·H_2O and H_2hman and their Mo complexes (**1** and **2**) are shown in Figs. 5–8.

4. Conclusion

Four dioxomolybdenum complexes of four different ONO donor hydrazones were synthesized and characterized using various physicochemical techniques. Conductivity values showed the non-electrolytic nature of complexes, and magnetic studies revealed diamagnetic nature showing the existence of +6 oxidation state of Mo in these complexes. Spectral studies help us to conclude that all complexes are dimeric in nature and in all cases ligands are in tri-coordinate dideprotonated forms. Thermal stability investigations of complexes enable us to evaluate the assumed positions of the water molecules in the inner or outer sphere of coordination.

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