

Synthesis and Characterization of Zn (II) and Mo (VI) Complexes of Schiff Base Derived from 2-Hydroxy-4-Methoxyacetophenone

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Abstract: The four complexes of zinc (II) and molybdenum (VI) with Schiff base derived from acylhydrazones have been prepared and characterized by elemental analysis, IR, ¹H-NMR, thermal analysis and molar conductance studies. Both the two free hydrazones (ligands) that were synthesized acts as a tridentate dianionic ONO donor towards the four complex centers. The conductance measurements in DMF of all the four metal complexes, suggest that they are non-electrolytes. Singlets found in the region 12-14 ppm of the free hydrazones indicates the present of iminol in solution. Also the NMR of zinc complexes was not as a result of its poor solubility. In the FTIR spectra of the free hydrazones, the bands due to carbonyl group were observed in the region 1630-1650cm⁻¹ and these are absent in the spectra of the complexes suggesting enolization and deprotonation of ligands, whereas for the metal complexes, in compounds A and C broad bands observed at 3409 and 3417cm⁻¹ indicates the present of lattice water. In the thermal analysis, there is a weight loss due to lattice in compound A and C.

Keywords: Schiff Base, Ligand, Complex, Molybdenum, Zinc

1. Introduction

Coordinating complex or metal complex consists of a central atom or ion, which is usually metallic and is called coordination center, and surrounded by molecules or ions that are in turn known as ligands. For the formation of complex the central metal ion must have an empty orbital of suitable energy while the ligand must have a lone pair of electron [1]. Schiff base compounds are condensation products of primary amines and carbonyl compounds [2] and were discovered by a German chemist Hugo Schiff in 1864 [3-4]. Schiff base possess functional group containing carbon-nitrogen double bond with the nitrogen atom linked to an aryl or alkyl group, with the exception of hydrogen [5]. Schiff base ligands have played an essential role in the development of coordination chemistry [6] due to their ability to form a stable

complexes with different transition metal ions and lanthanide metal ions in a various oxidation state through nitrogen and oxygen atoms [7]. According to [8] some compounds have a functional group that contain a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group, rather than hydrogen. It has been known that a variety of metal ions on interaction with Schiff bases yield chelates. Transition metal Schiff base complexes have been found to play a vital role in medicine, biological systems and industries [9]. Wail and Young [10] and Siraj and Sambo [11] reported that Schiff bases can accommodate different metal centers involving various coordination modes in which the homo and hetero metallic complexes with varied stereochemistry have been synthesized. Schiff bases derived from hydrazones and aroyl hydrazines have been widely used as ligand for the synthesis of transition metal complexes. Schiff bases or

their metal complexes have many applications in different fields. Hydrazones, heteroaroyl hydrazones ligands and their metal complexes are biologically active [12]. Recently there has been a considerable interest in the coordination chemistry of transition metals especially, zinc and molybdenum with O-N donor hydrazone ligands because of their potential biological and pharmacological applications. Acylhydrazones and their transition metal complexes are very promising compounds in this field and their crystal structures and spectral investigations are well desirable. These metals (Zn (II) and Mo (VI)) have strong ability to form complexes with proteins, peptides, amino acids, hydrazones as well as other organic substances in the living organisms.

2. Materials and Methods

2.1. Chemicals and Solvents

Nicotinic acid hydrazide (Aldrich) and Benzhydrazide (Aldrich), $\text{MoO}_2(\text{acac})_2$ (Aldrich) 2,2'-bipyridine (LOBA

Chemie), 1,10-phenanthroline (LOBA Chemie) and Zn $(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (S. D. Fine) were used without further purification. Solvents used were ethanol and methanol (Aldrich).

2.2. Physical Measurements

C, H, and N analyses were performed by Perkin-Elmer 2400 instrument. FT-IR spectra ($4000\text{--}600\text{ cm}^{-1}$) as KBr discs of the samples were recorded on a JASCO-460 plus spectrophotometer. Electronic spectra were obtained using a CECIL CE7400, 7000 SERIES, UV/VIS spectrophotometer. Magnetic susceptibility was measured with a Sherwood Scientific MSBMK1 sample magnetometer with Hg $[\text{Co}(\text{SCN})_4]$ as calibrant.

2.3. Syntheses of Ligands

All the ligands and their complexes were synthesized using a standard procedure as report [13-14]. The scheme for the synthesis of acylhydrazones is shown in Figure 1 below.

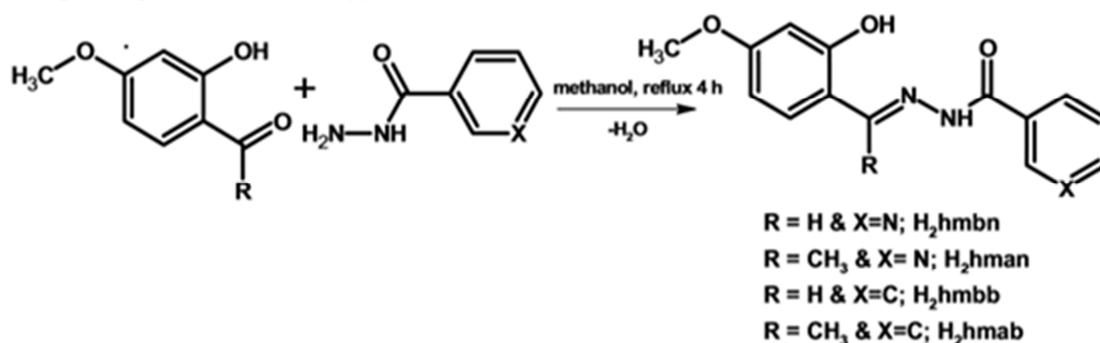


Figure 1. Schematic representation of the syntheses of acylhydrazones.

2.3.1. 2-Hydroxy-4-methoxyacetophenone

Nicotinoylhydrazone (H_2hman)

Nicotinic acid hydrazide (0.137 g, 1 mmol) dissolved in methanol was refluxed with 2-hydroxy-4-methoxyacetophenone (0.166 g, 1 mmol) in methanol in presence of a few drops of glacial acetic acid for 4 hours. On cooling colorless needle shaped compound was separated. Yield 70%. Elemental Anal. Found (Calcd.) (%): C, 62.94 (63.15); H, 5.39 (5.30); N, 14.46 (14.73).

2.3.2. 2-Hydroxy-4-methoxyacetophenone

Benzoylhydrazone (H_2hmab)

Benzhydrazide (0.136 g, 1 mmol) dissolved in methanol was refluxed with 2-hydroxy-4-methoxyacetophenone (0.166 g, 1 mmol) in methanol in presence of a few drops of glacial acetic acid for 4 hours. On cooling colorless needle shaped compound was separated. Yield 68%. Elemental Anal. Found (Calcd.) (%): C, 67.25 (67.59); H, 5.61 (5.67); N, 9.68 (9.85).

2.4. Syntheses of Zinc (II) and Mo (VI) Complexes

$[\text{Zn}(\text{hman})]_2 \cdot \text{H}_2\text{O}$ (A): Zn $(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.219 g, 1 mmol) in methanol was added to the H_2hman solution in

methanol (0.285 g, 1 mmol) and stirred for about two hours. The yellow product formed was filtered, washed with methanol, followed by ether and dried over P_4O_{10} in vacuo. Elemental Anal. Found (Calcd.) (%): C, 50.90 (50.37); H, 3.58 (3.94); N, 11.75 (11.75).

$[\text{Zn}(\text{hmab})]_2$ (B): Methanolic solutions of the H_2hmab (0.284 g, 1 mmol) and Zn $(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.219 g, 1 mmol) were mixed and stirred for about 2 hours. The product separated was yellow colored and it was filtered, washed with methanol, followed by ether and dried over P_4O_{10} in vacuo. Elemental Anal. Found (Calcd.) (%): C, 54.89 (55.27); H, 3.59 (4.06); N, 7.9C9 (8.06).

$[\text{MoO}_2(\text{hman})]_2 \cdot \text{H}_2\text{O}$ (C): To the H_2hman solution in methanol (0.285 g, 1 mmol), methanolic solution of $\text{MoO}_2(\text{acac})_2$ (0.326 g, 1 mmol) was added. The resulting solution has an orange color and it was refluxed for four hours. The orange colored product formed was filtered, washed with methanol, followed by ether and dried over P_4O_{10} in vacuo. Elemental Anal. Found (Calcd.) (%): C, 42.85 (42.87); H, 3.20 (3.36); N, 10.17 (10.00).

$[\text{MoO}_2(\text{hmab})]_2$ (D): Methanolic solutions of the H_2hmab (0.284 g, 1 mmol) and $\text{MoO}_2(\text{acac})_2$ (0.326 g, 1 mmol) were mixed and refluxed for about 4 hours. The

product separated was orange colored and it was filtered, washed with methanol, followed by ether and dried over P_4O_{10} in vacuo. Elemental Anal. Found (Calcd.) (%): C, 46.14 (46.84); H, 3.32 (3.44); N, 6.86 (6.83).

3. Result and Discussion

3.1. Acylhydrazones Ligands

All the two acylhydrazones were synthesized in a very superficial and identical way and all the synthesized acylhydrazones act as tridentate ligands during the synthesis of their metal complexes

3.1.1. 1H NMR Spectral Studies

The 1H NMR spectrum of an organic compound provides effective information concerning the number of different types of hydrogen present in the molecule, the relative numbers of the different types of hydrogen, the electronic environment of the different types of hydrogen and also the number of hydrogen 'neighbor' a hydrogen has. Here the 1H NMR spectra of the two hydrazones were taken in DMSO.

H_2hman : In the 1H NMR spectrum of the compound, OH and iminol protons gave sharp singlets at 11.43 ppm and 13.56 ppm respectively with a peak area corresponds to one each. These assignments are confirmed by D_2O exchange studies. During D_2O exchange the intensity of these peaks are considerably reduced. Here the methoxy protons gave a singlet at 3.78 ppm and the methyl protons show a singlet at 2.45 ppm. Here also the aromatic protons show multiplets in the region of 6-9.5 ppm. Figure 2 shows the 1H NMR spectrum of the compound.

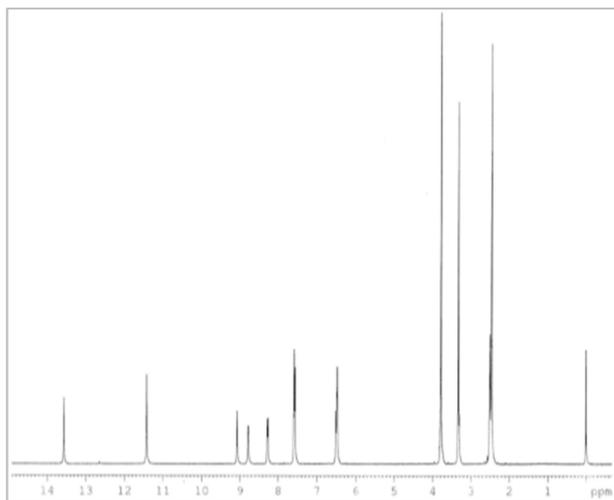


Figure 2. 1H NMR Spectrum of H_2hman .

H_2hmab : The 1H NMR spectrum of the compound is shown in Figure 3. The singlet observed at 13.65 ppm is assigned to proton attached to iminol oxygen and singlet peak observed at 11.22 ppm is assigned to phenolic proton. Both of them have peak area corresponds to one. These assignments are confirmed by deuterium exchange studies.

Here the methoxy protons gave a singlet at 3.76 ppm and the methyl protons show a singlet at 2.43 ppm. Here also the aromatic protons show multiplets in the region of 6-8 ppm.

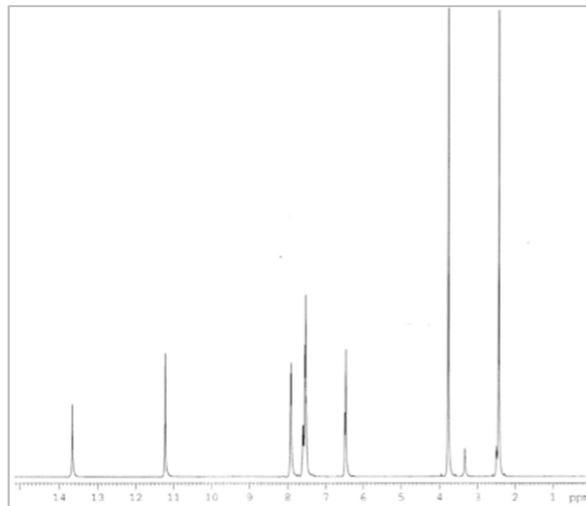


Figure 3. 1H NMR Spectrum of H_2hmab .

3.1.2. Infrared Spectral Studies

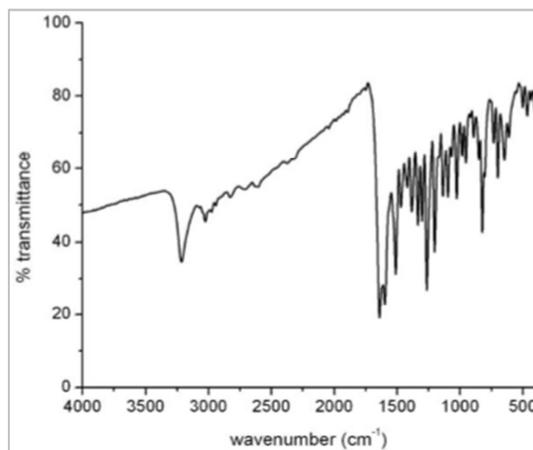


Figure 4. IR Spectrum of H_2hman .

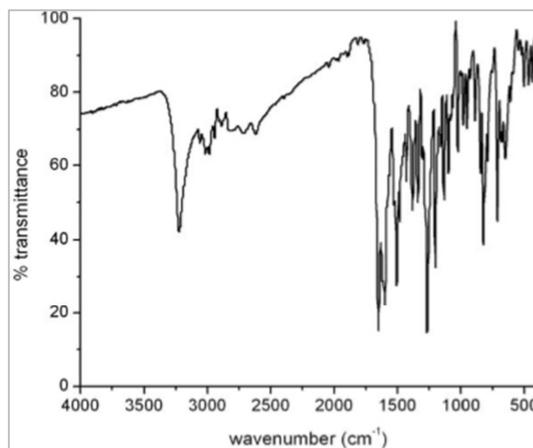


Figure 5. IR Spectrum of H_2hmab .

The characteristic bands of different functional groups

provide valuable information regarding the structure. Table 1 lists the main vibrational bands of the hydrazones. In H_2hmbn , H_2O a band is observed at 3382 cm^{-1} which is due to the presence of lattice water in the molecule. In the remaining compounds there are no bands in this region due to the absence of water molecules. In all the four hydrazones, a band observed around 3200 cm^{-1} is assigned to phenolic O—H and N—H groups gave bands around 3050

cm^{-1} . A strong band is observed in between $1630\text{--}1650\text{ cm}^{-1}$ which indicates the presence of carbonyl group in these compounds. The azomethine bands are observed around 1600 cm^{-1} [15]. The C—O stretching is observed around 1275 cm^{-1} . The N—N stretching vibrations are found in between 1110 and 1140 cm^{-1} . Figures 4-5 show the infrared spectra of the four hydrazones.

Table 1. Selected IR frequencies (cm^{-1}).

| Ligand | V (O-H) | V (N-H) | V (C=O) | V (C=N) | V (N-N) | V (C-O) |
|--------------------|---------|---------|---------|---------|---------|---------|
| H_2hman , H_2O | 3219 | 3029 | 1638 | 1602 | 1135 | 1262 |
| H_2hmab | 3326 | 3025 | 1650 | 1601 | 1127 | 1265 |

3.2. Zinc (II) and Molybdenum (VI) Complexes

3.2.1. Molar Conductivity

The experimental and calculated analytical data of all the four Zn (II) and Mo (VI) complexes are in close agreement. Magnetic susceptibility studies indicate diamagnetic nature of these complexes and it indicates the d^{10} outer electronic configuration of zinc, it is also an evidence for molybdenum is in +6 oxidation state. The molar conductivity measured for all the four complexes in 10^{-3} M DMF solution was found to be below $15\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ which is much less than the value of $65\text{--}90\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ obtained for a 1:1 electrolyte in the same solvent [16]. So the conductance measurements in DMF suggest that they are non-electrolytes. The Table 2 below present the molar conductivity measurement.

Table 2. Molar conductivity measurements.

| | | |
|---|------------------------------|----|
| A | $[Zn(hman)]_2 \cdot H_2O$ | 10 |
| B | $[Zn(hmab)]$ | 09 |
| C | $[MoO_2(hman)]_2 \cdot H_2O$ | 04 |
| D | $[MoO_2(hmab)]_2$ | 05 |

#molar conductivity (in $\text{mho cm}^2\text{ mol}^{-1}$) taken in 10^{-3} DMF.

3.2.2. Infrared Spectra

Significant IR spectral bands of the complexes are listed in Table 3. Free ligands show strong absorptions in the $1630\text{--}1650\text{ cm}^{-1}$ region which are assigned to carbonyl group, and bands due to azomethine group were observed around 1600

cm^{-1} . In compound 4, broad bands were observed at 3409 and 3417 cm^{-1} due to lattice water. Coordination of hydrazones to the zinc ion through the azomethine nitrogen atom is expected to reduce the electron density in the azomethine link and thus, lower the $\nu(\text{C=N})$ absorption frequency. Hence this band undergoes a shift to lower wavenumber [16]. Also in complex 4, a lower shift is observed in $\nu(\text{C=N})$ absorption frequency indicates coordination of azomethine nitrogen to zinc. Coordination of azomethine nitrogen is also evident from the increase in N—N stretching frequency in all the complexes. In complex B, bands correspond to carbonyl groups are absent suggesting the enolization of ligands during complexation. But in compound A bands observed around 1645 and 3000 cm^{-1} are assigned to carbonyl group and NH group respectively, i.e in this complex, ligand is in the amido form. For the compound A, bands at 1600 and 1386 cm^{-1} correspond to symmetric and asymmetric vibrations of the acetate group are consistent with the presence of a unidentate acetate group [15]. In compound 3, a very intense band is observed at 1600 cm^{-1} , is a combination band of $\nu(\text{C=N})$ and $\nu_a(\text{CH}_3\text{COO})$ stretching frequencies. For all the complexes, phenolic C—O stretching occurs at lower wavenumber when compared to that of the ligands indicating the deprotonation and coordination of phenolic OH. Appearance of new bands in the regions of $525\text{--}560$ and $440\text{--}460\text{ cm}^{-1}$ are assignable to $\nu(\text{Zn-O})$ and $\nu(\text{Zn-N})$ respectively. The IR spectra of the complexes are shown in the Figures 6-7.

Table 3. Selected IR bands (cm^{-1}) with speculative assignments of Zn (II) complexes (newly formed).

| Ligand | V (O-H) | V (N-H) | V (C=O) | V (C=N) | V (Zn--) | V (Zn-N) |
|-------------------------------|---------|---------|---------|---------|----------|----------|
| $[Zn(hman)]_2 \cdot H_2O$ (A) | 1597 | 1524 | 1161 | 1244 | 547 | 445 |
| $[Zn(hmab)]_2$ (B) | 1593 | 1540 | 1150 | 1223 | 540 | 459 |

Table 4. Selected IR bands (cm^{-1}) with speculative assignments of Mo (VI) complexes (newly formed).

| Compounds | V (C=N) | V (C=N) ² | V (N-N) | V (C-O) | V (Mo=O) | V (Mo=OMo) |
|------------------------------|---------|----------------------|---------|---------|----------|------------|
| $[MoO_2(hman)]_2 \cdot H_2O$ | 1593 | 1532 | 1140 | 1249 | 913,942 | 854 |
| $[MoO_2(hman)]_2$ | 1597 | 1549 | 1156 | 1290 | 913,942 | 854 |

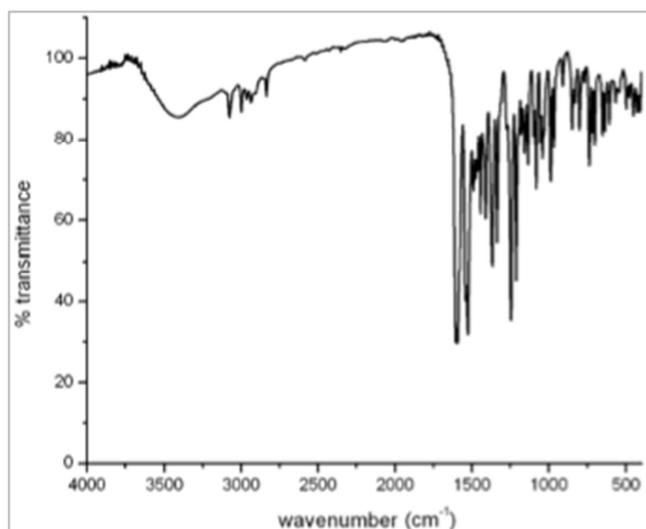


Figure 6. IR-Spectrum of $[Zn(hman)]_2 \cdot H_2O$ (A).

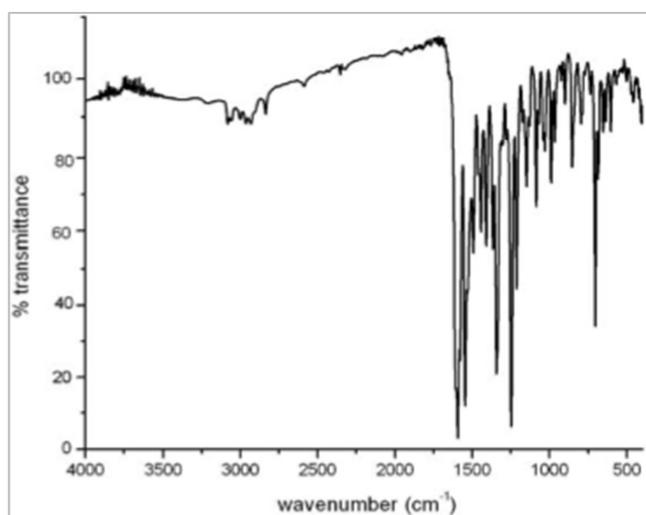


Figure 7. IR-Spectrum of $[Zn(hmab)]_2$ (B).

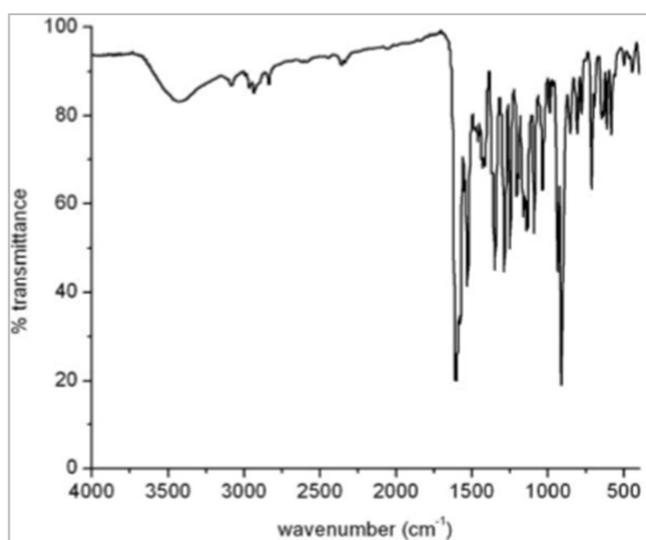


Figure 8. IR-Spectrum of $[MoO_2(hman)]_2 \cdot H_2O$ (C).

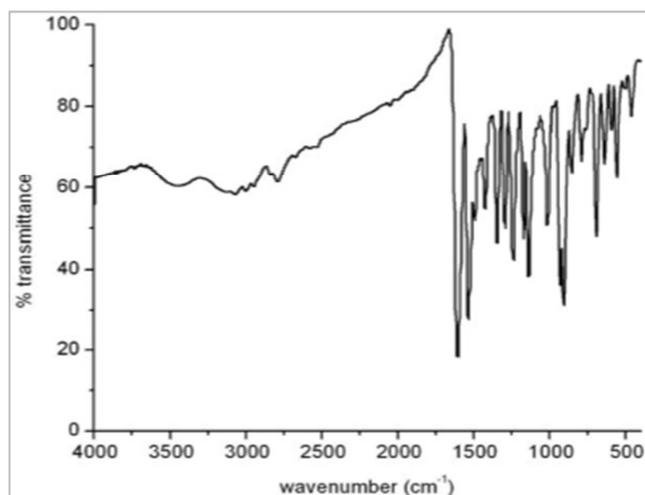


Figure 9. IR-Spectrum of $[MoO_2(hmab)]_2$ (D).

3.2.3. 1H NMR Spectral Studies

In the case of diamagnetic Mo (VI) complexes the coordination of ligands to the metal centre is substantiated by 1H NMR spectral studies of the ligands and complexes, in DMSO solution. Singlets found in the region 12-14 ppm due to iminol protons in free hydrazones were not found in the spectra of complexes indicate the coordination of iminol oxygen to metal center. Similarly singlets due to OH proton were found in-between 11 ppm and 12 ppm in free hydrazones were also absent in the spectra of complexes indicate the coordination of phenolic oxygen to metal centre. This leads to the conclusion that the hydrazones are coordinated in all the complexes in a dianionic form suggesting the ONO coordination to molybdenum. The singlets with an area integral of three in the range of 3-3.8 ppm indicate the presence of three methoxy hydrogens in free acylhydrazones were slightly shifted upon complexation. Multiplets for aromatic protons were found in the region 6-8 ppm in ligands do not show much shift in complexes. The 1H NMR spectra of the complexes are shown in the Figures 10-11.

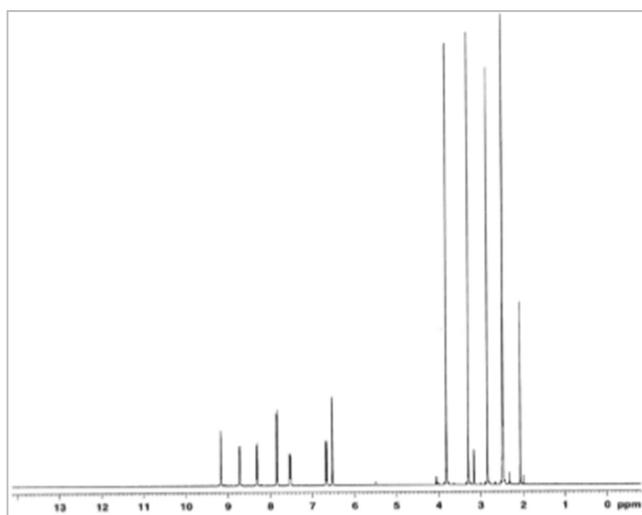


Figure 10. 1H NMR Spectra of $[MoO_2(hman)]_2 \cdot H_2O$ (C).

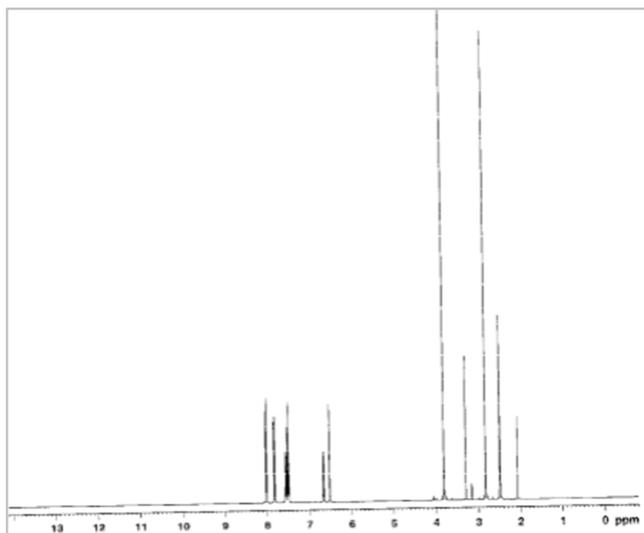


Figure 11. ^1H NMR Spectra of $[\text{MoO}(\text{hmab})]_2$ (D).

3.2.4. Thermal Analyses

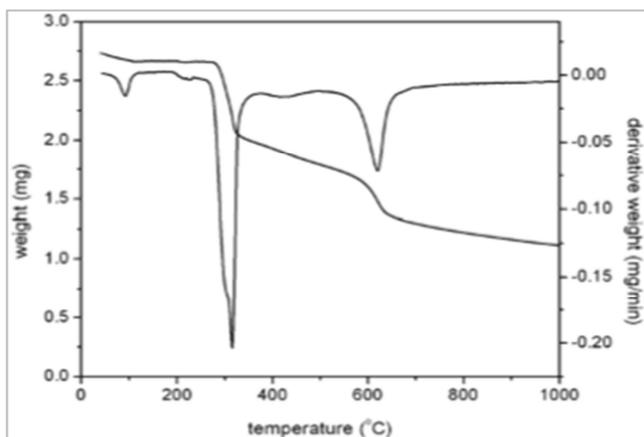


Figure 12. TG-DTG plot of $[\text{MoO}_2(\text{hman})]_2 \cdot \text{H}_2\text{O}$ (C).

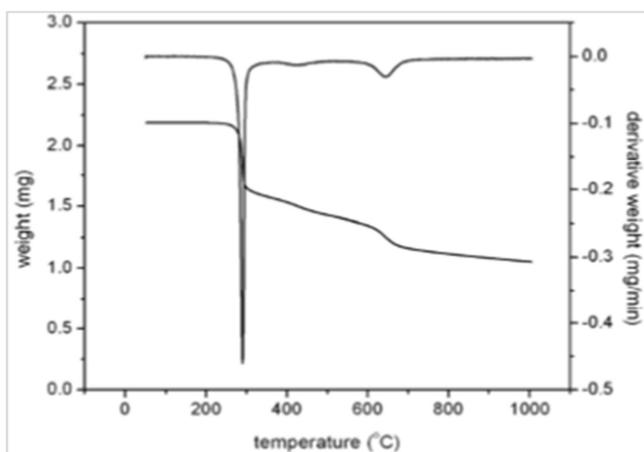


Figure 13. TG-DTG plot of $[\text{MoO}_2(\text{hmab})]_2$ (D).

In complex A, there is a weight loss below 120°C indicating the presence of lattice water. Whereas in complex B, no weight loss is observed in between 50-250°C indicating absence of water molecules in this complex.

Above 400°C the complexes begin to decompose and the decomposition was not seen to be completed even at 1000°C.

In molybdenum, the complex C showed loss of weight corresponds to one water molecule in the temperature range 80-110°C indicate the presence of lattice water in this complex. Whereas complex D, showed no weight loss in the region below 250°C and this indicated the absence of water molecule. All the complexes decompose over 250°C. TG-DTG curves of the complexes are shown in Figures 12-13.

4. Conclusion

The four new complexes of zinc and molybdenum prepared using different acylhydrazones derived from 2-hydroxy-4-methoxyacetophenone were characterized. Both the two free hydrazones (ligands) that were synthesized acts as a tridentate dianionic ONO donor towards the eight complex centers. The conductance measurements in DMF of all the four metal complexes, suggest that they are non-electrolytes. Singlets found in the region 12-14 ppm of the free hydrazones indicates the present of iminol in solution. Also the NMR of zinc complexes was not as a result of its poor solubility. In the FTIR spectra of the free hydrazones, the bands due to carbonyl group are observed in the region 1630-1650 cm^{-1} and these are absent in the spectra of the complexes suggesting enolization and deprotonation of ligands, whereas for the metal complexes, in compounds A and C broad bands observed at 3409 and 3417 cm^{-1} indicates the present of lattice water. In the thermal analysis, there is a weight loss due to lattice in compound A and C.

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