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### Synthesis and Spectroscopic Studies of Two New Complexes Containing Fe (III) and Mo (VI) of Two Tridentate ONO Donor Sets Ligands

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#### ABSTRACT

Two new Schiff bases  $HL^1$ : (E)-N-(1-(2-hydroxyphenylethylidene)benzohydrazide and  $HL^2$ : (E)-N-((2-hydroxynaphthalen-3-yl) methylene)benzohydrazide and their complexes with Fe(III) and Mo(VI) ions have been synthesized and characterized by elemental analysis, IR and UV-Vis spectroscopy,  $^1H$  NMR and  $^{13}C$  NMR. The analysis for the obtained products are consistent very well with the corresponding formula and the complexes were found to have the general formula  $[Fe(L^1)_2Cl]$ ,  $[MoO_2(L^2CH_3OH)Cl]$  and  $[MoO_2(L^1CH_3OH)Cl]$ . The data obtained show that Schiff bases were interacted with Fe (III) and Mo (VI) ions as a tridentate ligands with ONO donor group. Octahedral geometrical structure was proposed for complexes.

**Key words:** Schiff base complex, ONO tridentate ligands, Fe (III) complex, Mo (VI) complex.

#### INTRODUCTION

Schiff bases are easily prepared by the condensation of salicylaldehyde and its derivatives with primary amines represent an important class of chelating ligands [1]. They offer a versatile and flexible series of ligands capable to bind with transition, non- transition, lanthanide and actinide metal ions to give complexes with suitable properties for theoretical studies and practical applications [2-4]. Schiff bases and their metal complexes have been synthesized and studied because of their interesting and important properties such as their ability to reversibly to bind oxygen[5] and also their ability to stabilize different metals in various oxidation states and controlling the performance of metals in a large variety of useful catalytic transformation[6-13]. Metal complexes of Schiff bases have found diverse applications in addition to interesting structural chemistry [14]. They play an important role in the development of coordination chemistry related to catalysis, enzymatic reactions, magnetism, and molecular architectures [15].

#### MATERIALS AND METHODS

##### 2. Experimental

##### 2.1. Materials and physical measurements

All the chemicals were purchased from Merck Co. and were used as such. UV-Vis spectra were recorded on a Perkin Elmer Lambda25 in the range 200-700 nm. FT-IR spectra obtained as potassium bromide pellets in the range 400-4000  $cm^{-1}$  with a Nicolet-Impact 400D spectrometer. NMR spectra were acquired on a Bruker DRX400

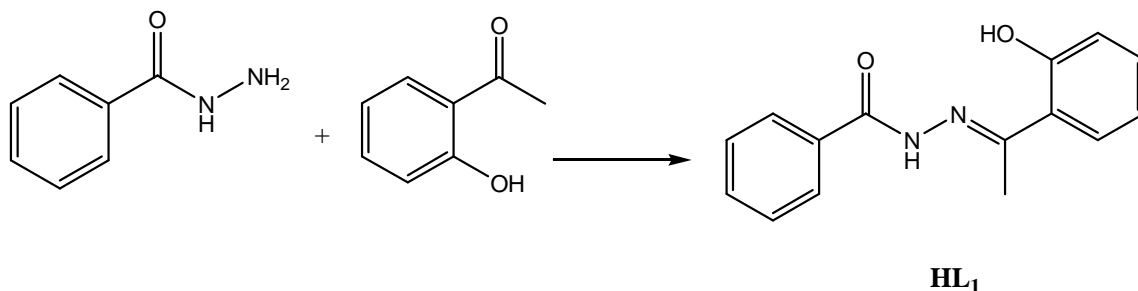
spectrometer operating at 400 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  NMR in DMSO as a solvent. All solution NMR chemical shifts are reported in parts per million (ppm) and coupling constants (J) in Hertz (Hz).

## 2.2. Syntheses of HL<sup>1</sup> and HL<sup>2</sup> Schiff base ligands

The HL<sup>1</sup> and HL<sup>2</sup> Schiff base ligands (Scheme1 and Scheme2) were prepared from the condensation of the amine with the corresponding aldehyde, using ethanol as a solvent. These ligands were characterized by elemental analysis, FT-IR and UV-Vis spectroscopy,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR.

### 2.2.1 Synthesis of HL<sup>1</sup>

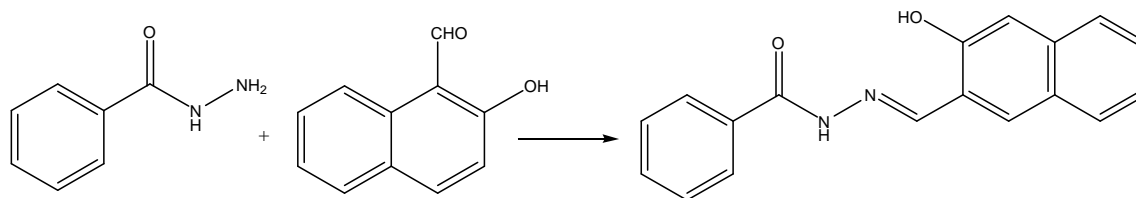
The ligand HL<sup>1</sup> was synthesized by refluxing a mixture of 1 mmol (0.136 g) of benzohydrazide with 1 mmol (0.12 mL) of 2-hydroxyacetophenone in ethanol as a solvent. After 4 h, the white precipitate was filtered, washed with 10 mL ethanol and dried at room temperature. The pure crystalline Schiff base was obtained in a good yield (72%). The melting point of the ligand is in the range of 182-184°C.



**Scheme1. Preparation of HL<sup>1</sup> ligand**

### 2.2.2 Synthesis of HL<sup>2</sup>

The ligand HL<sup>2</sup> was synthesized by adding 1 mmol (0.3124 g) of 2-hydroxy-1-naphtaldehyde in chloroform to 1 mmol (0.136 g) of benzohydrazide in ethanol under reflux condition. After 3 h the yellow-greenish precipitate was filtered, washed with ethanol and dried under air condition. The Schiff base was obtained in a good yield (90%). The melting point of this ligand is in the range of 220- 222°C.



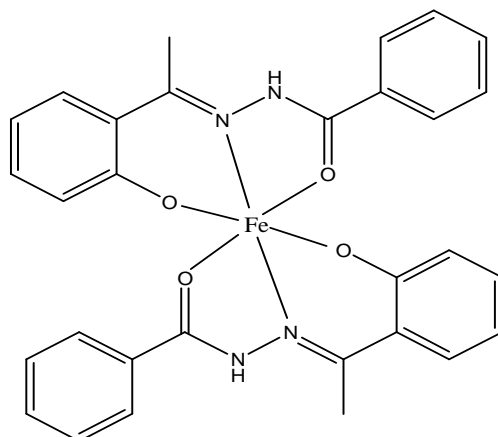
**Scheme 2. Preparation of HL<sup>1</sup> ligand**

## 2.3. Synthesis of Complexes

The complexes (Scheme3 and Scheme4) were prepared by refluxing ethanolic solutions of equimolar quantities of iron (III) chloride hexahydrate or  $\text{MoO}_2(\text{acac})_2$  with the corresponding ligand for 4h. These complexes were characterized by elemental analysis, FT-IR, UV-vis and atomic absorption spectroscopy, cyclic voltametry,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy.

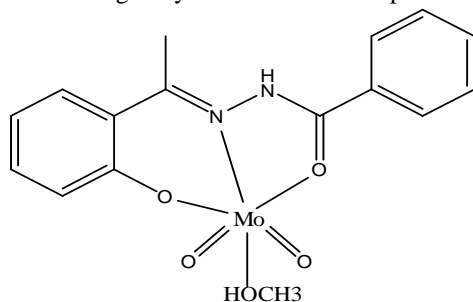
### 2.3.1. Synthesis of $[\text{Fe}^{\text{III}}(\text{L}^1)_2]$

The  $\text{Fe}^{\text{III}}(\text{L}^1)_2$  complex was obtained by adding the hot solution of iron (III) chloride hexahydrate in EtOH to the boiling ethanolic solution of HL<sup>1</sup> solution. A fine brown precipitate was immediately formed and kept under refluxing for 4h. After cooling the solution, the precipitate was filtered and washed with a small portion of ethanol. This complex was obtained in a good yield 54%. The melting point of this complex is in the range of 297- 300°C.

Scheme3. The structure of complex  $[\text{Fe}^{\text{III}}(\text{L}^1)_2]$ 

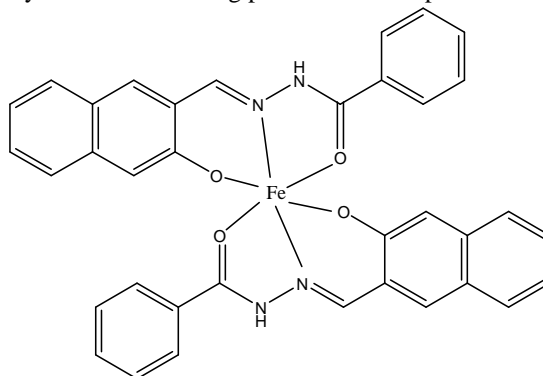
### 2.3.2. Synthesis of $[\text{MoO}_2\text{L}^1(\text{MeOH})]\text{Cl}$

This complex was synthesized under reflux in MeOH as solvent. In this order 1 mmol of  $\text{MoO}_2(\text{acac})_2$  in MeOH was added to the 1 mmol of the boiling Schiff base in MeOH. A brown precipitate was formed. The mixture was under reflux for 4h. Then it was cooled and the precipitate was filtered and washed with a small portion of methanol and diethyl ether. This complex was obtained in a good yield 65%. This complex decomposed in  $250^\circ\text{C}$ .

Scheme3. The structure of  $[\text{MoO}_2(\text{L}^1)\text{CH}_3\text{OH}]\text{Cl}$  complex

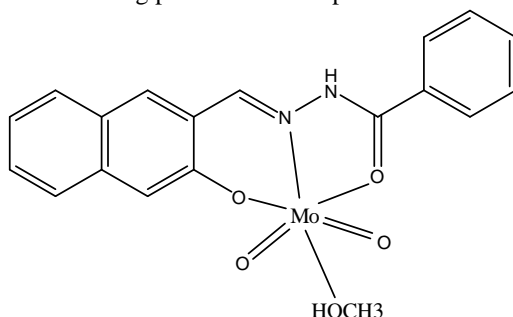
### 2.3.3 Synthesis of $[\text{Fe}^{\text{III}}(\text{L}^2)_2]\text{Cl}$

The complex was obtained by adding the hot solution of iron (III) chloride hexahydrate in EtOH to the boiling ethanolic solution of Schiff base in a molar ratio of 1:2, respectively. A fine brown precipitate was immediately formed and kept under refluxing for 4h. After cooling the solution, the precipitate was filtered and washed with a small portion of ethanol and diethyl ether. The melting point of this complex is in the range of  $330-332^\circ\text{C}$ .

Scheme4. The structure of  $[\text{Fe}^{\text{III}}(\text{L}^2)_2]\text{Cl}$  complex

### 2.3.4 Synthesis of $[\text{MoO}_2\text{L}^2(\text{MeOH})]\text{Cl}$

The Mo complex was synthesized in MeOH under reflux condition. 1 mmol of  $\text{MoO}_2(\text{acac})_2$  in MeOH was added to the 1 mmol of the Schiff base in MeOH under reflux. A fine orange precipitate was immediately formed and kept under refluxing for 4 h. The mixture was cooled and the precipitate was filtered and washed with a small portion of methanol and diethyl ether. The melting point of this complex is 317- 318°C.



Scheme5. The structure of  $[\text{MoO}_2\text{L}^2(\text{MeOH})]\text{Cl}$  complex

## RESULTS AND DISCUSSION

### 3.1. Electronic spectra

UV- Vis spectrum ( $>200$  nm) of  $\text{HL}^1$  and  $\text{HL}^2$  in methanol consist of a band appears in 324.9 and 324.2 nm, assigned to a  $\pi \rightarrow \pi^*$  transition respectively, and a band at 361.4 nm in  $\text{HL}^2$ , refer to  $n \rightarrow \pi^*$  excitation of the azomethine group. After complexation with Fe(III) and Mo(VI), several transitions corresponding to interligand  $\pi \rightarrow \pi^*$  transitions appear in lower energy (below 350 nm). These result show the imine group nitrogen atom has been coordinated to the metal ion [16, 17]. The observed bands at about 280- 320 nm are assigned as  $\pi \rightarrow \pi^*$  type transitions involving molecular orbitals located on the phenolic chromophore. The bands at 396.7 and 227.0 nm in  $[\text{Fe}^{\text{III}}(\text{L}^1)_2]\text{Cl}$  and  $[\text{Fe}^{\text{III}}(\text{L}^2)_2]\text{Cl}$  refers to LMCT ( $\pi_{\text{Cl}} \rightarrow d_{\text{Fe}}$ ) respectively. These bands in Fe(III) and Mo(VI) complexes appear at 312- 319 nm and 300- 314 nm respectively. This blue shift in the complexes may be due to the donation of a lone pair of electrons by the oxygen of the phenoxy group to the central metal atom [18, 19].

### 3.2. IR spectra

The IR spectrum of the ligand exhibits a broad band characteristic of the OH group at 2500-3400  $\text{cm}^{-1}$  which is assigned to the intramolecular H-bonding vibration ( $\text{O}-\text{H} \cdots \text{N}$ ). The IR spectrum of Fe (III) complex shows a characteristic medium intensity absorption band in 3444  $\text{cm}^{-1}$ , which is refers to water molecule [19, 20]. The phenolic C—O band of  $\text{HL}^2$  at 1293  $\text{cm}^{-1}$  shifts to 1201  $\text{cm}^{-1}$  in Fe(III) complex and  $\text{cm}^{-1}$  in Mo(VI) complex respectively because of the O—M band formation(M: Fe(III) and Mo(VI)). The C=N band of HL at 1616  $\text{cm}^{-1}$  shifts to 1600  $\text{cm}^{-1}$  in Fe(III) complex and 1596  $\text{cm}^{-1}$  in Mo(VI) complex correspondingly due to the loss of hydrogen bonding and the formation of a new chelate ring between the imine nitrogens and the metal ions[17]. It is noticeable that the Mo=O bands are also observed at 908 and 945  $\text{cm}^{-1}$  in Mo (VI) complex [21-23].

### 3.3. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

The  $^1\text{H}$  NMR spectrum of the Schiff base shows the presence of an azomethine and a phenolic group. A sharp singlet at 9.49 ppm (s, 1) which be rationalized to the azomethine proton in  $\text{HL}^2$  shifts downfield and appears at 9.78 ppm (s, 1), resulting from the coordination of the azomethine nitrogen [23]. Two signals that are recorded in 11.34 ppm (s, 1) and 13.37 ppm (s, 1) in  $\text{HL}_1$  and 12.22 ppm (s, 1) and 12.78 (s, 1) in  $\text{HL}_2$  refer to and O—H and N—H protons respectively. The emission of O—H in the spectra of the Mo complexes indicates the coordination to Mo atom. The aromatic protons are recorded in 6.87-7.94 ppm (m, 9) in  $\text{HL}^1$  and 7.23-9.49 ppm (m, 11) in  $\text{HL}^2$ . The  $^{13}\text{C}$  NMR spectrum of the Schiff base show the signals in 158.58 ppm, 159.24 ppm and 164.88 ppm in  $\text{HL}^1$  and 147.32 ppm, 158.51 ppm and 162.99 ppm in  $\text{HL}^2$  that are recorded for imine C=N, phenolic C—O and carbonyl C=O functional groups respectively. The absence of phenolic C—O in the spectra of the Mo complexes indicates the coordination of the phenolic oxygen atom(s) to metal after proton replacement

## CONCLUSION

The synthesis of HL<sup>1</sup>, HL<sup>2</sup> ligands, Fe(III) and Mo(VI) complexes were achieved by high purification in regards to their UV-Vis, FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra. According to the several papers these types of ligands are very important in coordination chemistry. HL<sup>1</sup>, HL<sup>2</sup> ligands and their complexes have too much application.

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