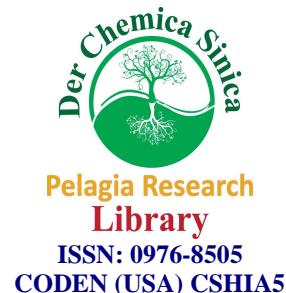




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### Synthesis and Characterization of a New Poly (amidoamine) Dendrimer-like Iron (III) and Molybdenum (VI) Complexes

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#### ABSTRACT

A new dendrimer-like Schiff base H<sub>2</sub>L and its complexes with Fe (III) and Mo (VI) have been synthesized and characterized by <sup>1</sup>H NMR, FT- IR and UV-Vis spectroscopy. The analysis for the obtained products are consistent very well with the corresponding formula and the complexes were found to have the general formula [FeLCl(MeOH)] and [MoO<sub>2</sub>L]. The data obtained show that Schiff base was interacted with Fe (III) and Mo (VI) ions as a tetradentate ligand with N<sub>2</sub>O<sub>2</sub> donors. The distorted octahedral geometrical structure was proposed for complexes. The yields for Schiff base ligand, Fe (III) and Mo (VI) complexes are 98, 76 and 43 percent.

**Keywords:** Dendrimer, Molybdenum, Schiff base, Poly-amidoamine, Tetradentate ligand, Macromolecule.

#### INTRODUCTION

Dendrimers are highly branched molecules that consist of a simple organic molecule as a central core. They are synthesized through a stepwise and repetitive reaction, leading to unimolecular products [1]. It has proved that the strategies of Tomalia and co-workers [2,3], Frechet and co-workers [4-6], and Zimmerman and co-workers [7] were effective for synthesis of dendrimers and macromolecules [8]. Dendrimers are attractive molecules because of their multifunctional properties [9], and many of the researches are attention to these macromolecules due to their important applications in many cases such as liquid crystalline polymers, drug carriers especially for cancer therapy, modeling of enzymes, and etc [8,10]. Transition metal based on functionalized dendrimers are also very promising application such as effective catalysts [11-14].

#### MATERIALS AND METHODS

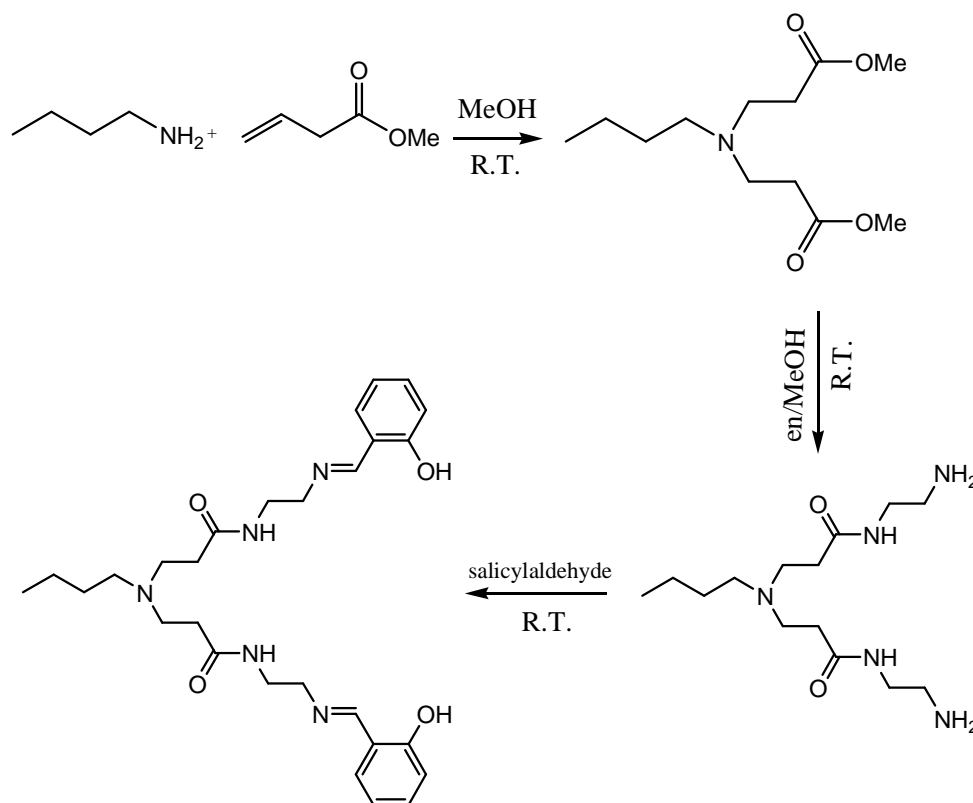
##### 2. Experimental

###### 2.1. Materials and Instruments

Salicylaldehyde, ethylenediamine, methylacrylate, acetylacetonate, n-buthylamine, nitric acid, absolute methanol, iron (III) chloride hexahydrate and ammonium heptamolibdate were purchased from Merck Co. UV-Vis spectra were recorded on a PerkinElmer Lambda25 in the range 200-700 nm. FT-IR spectra obtained as potassium bromide pellets in the range 400-4000 cm<sup>-1</sup> with a Nicolet-Impact 400D spectrometer. NMR spectra were recorded on Bruker advance DPX 400 MHz instrument.

## 2.2. Synthesis of the dendrimer-like Schiff base ligand[H<sub>2</sub>L]

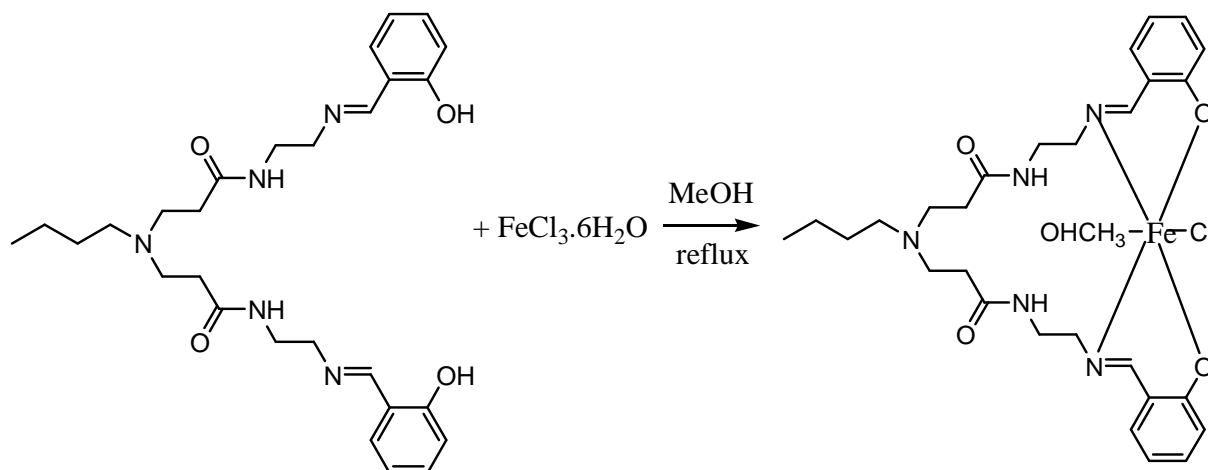
The dendrimer-like Schiff base ligand was synthesized according to the literature [15-17] with suitable modification as follows: 1 mmol (0.1 mL, 0.0731 g) of n-butylamine was added in portions to a 100 mL round bottom flask containing 250 mmol (23 mL, 21.5225 g) methyl acrylate in 20 mL MeOH as solvent at room temperature for 5 days [14]. After that, the bright colorless liquid cooled to 0 °C and was added to a mixture of 2 mmol (0.15 mL, 0.1202 g) of ethylenediamine in 20 mL MeOH and cooled to 0 °C. Then the mixture was warmed to room temperature and was stirred at room temperature for 5 days [8]. At this time, 2 mmol of salicylaldehyde in 5 mL MeOH was added drop wise to cooled reaction mixture. The flask was immediately warmed and a plentiful bright yellow precipitation was formed. The product was filtered and washed with a small portion of MeOH (Scheme 1). The Schiff base was obtained in a good yield (98%), its melting point is in the range of 125-128°C.



Scheme 1. Synthesis of the dendrimer-like Schiff base ligand

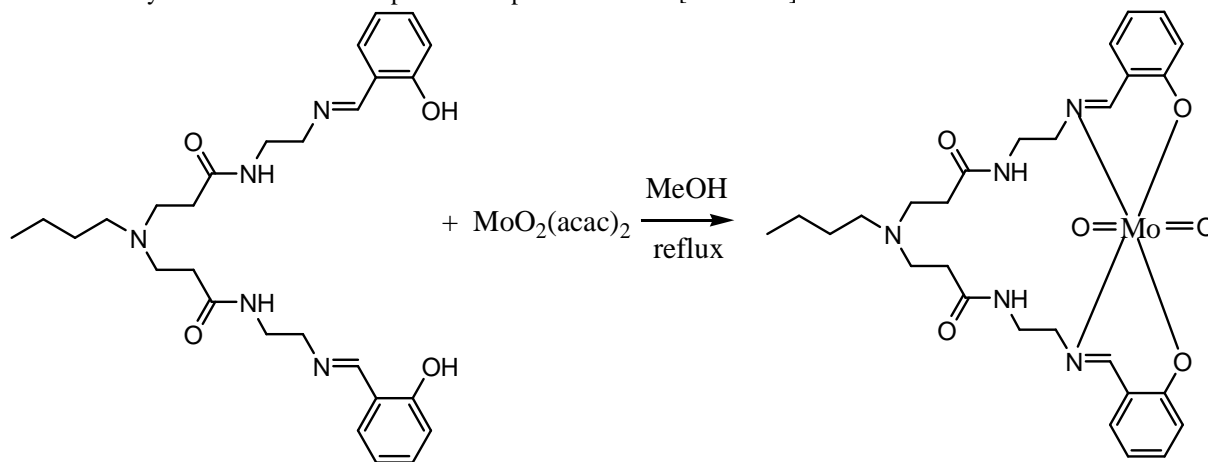
## 2.3. Synthesis of Iron (III) complex

The Iron (III) complex [Scheme 2] with this ligand was synthesized according to the reported procedure [14]. 0.5 mmol (0.2548 g) of the synthesized Schiff base ligand prepared as above were added to a 100 mL round bottom flask containing 20 mL MeOH as solvent. Then 0.5 mmol (0.1352 g) of FeCl<sub>3</sub>.6H<sub>2</sub>O in MeOH was added to the solution of the ligand under reflux condition. This mixture was refluxed for 4h. A pure brown precipitation was formed (scheme 2). The product was cooled, filtered, washed with a small portion of MeOH and dried under air condition. This product obtained in the yield of 76%. The melting point of this complex is in the range of 267-271°C.

Scheme 2. [FeLCl(CH<sub>3</sub>OH)] complex

#### 2.4. Synthesis of Mo (VI) complex

Synthesis of the MoO<sub>2</sub>(acac)<sub>2</sub> was achieved in according to the literature [15]. The Mo(VI) complex was synthesized by refluxing of a methanolic solutions of equimolar quantities of MoO<sub>2</sub>(acac)<sub>2</sub> with the ligand for 8h. In this order 0.5 mmol (0.1635 g) of MoO<sub>2</sub>(acac)<sub>2</sub> in MeOH was added to the 0.5 mmol (0.2548 g) of the boiling Schiff base in MeOH. A brown precipitate was formed (scheme 3). The mixture was under reflux for 8h. 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 yield of 43%. This complex decomposed in 183°C [Scheme 3].

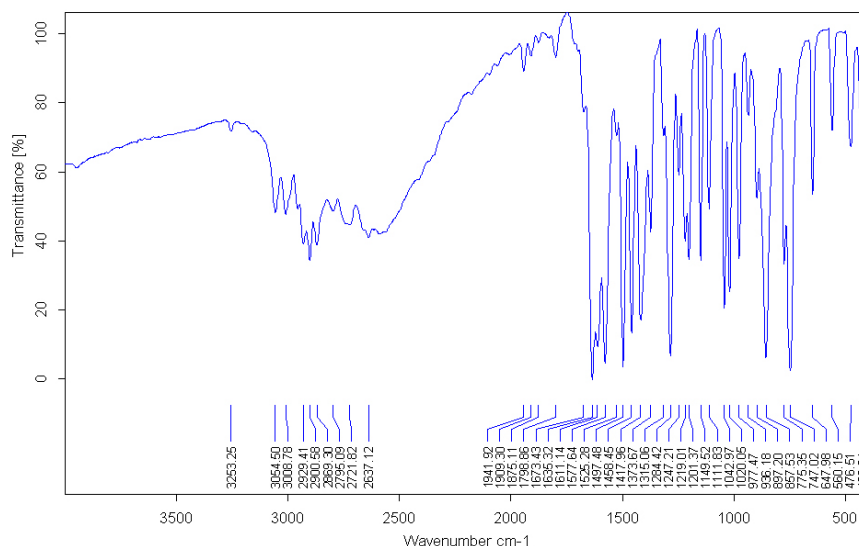
Scheme 3. [MoO<sub>2</sub>L] complex

### RESULTS AND DISCUSSION

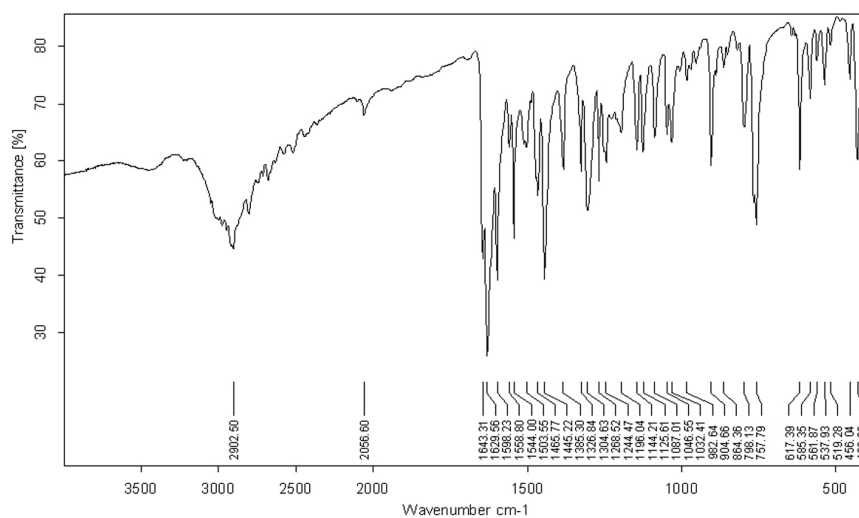
#### 3.1. FT-IR studies

H<sub>2</sub>L ligand was synthesized in 3 steps. In the first one, methylacrylate reacted with n-butylamine. In this case the FT-IR spectrum shows a sharp peak at 1740 cm<sup>-1</sup> referred to C=O group, and the peaks at 2666-2956 cm<sup>-1</sup> referred to aliphatic stretching C—H vibrations. In the second step, ethylenediamine reacted with the above synthesized product. The FT-IR spectrum exhibits two peaks at 3347 cm<sup>-1</sup> and 3288 cm<sup>-1</sup> that confirm the presence of NH<sub>2</sub> group. The peak related to C=O shifted to lower wave number and appear at 1650 cm<sup>-1</sup>. In the last step, salicylaldehyde was added to the above mixture. The FT-IR spectrum of this ligand recorded a broad band characteristic of the OH group at 2100-3200 cm<sup>-1</sup> which is assigned to the intramolecular H-bonding vibration (O—H...N) [16,17]. The C=O and the C=N bands of H<sub>2</sub>L were represented at 1635 cm<sup>-1</sup> and 1578 cm<sup>-1</sup> respectively.

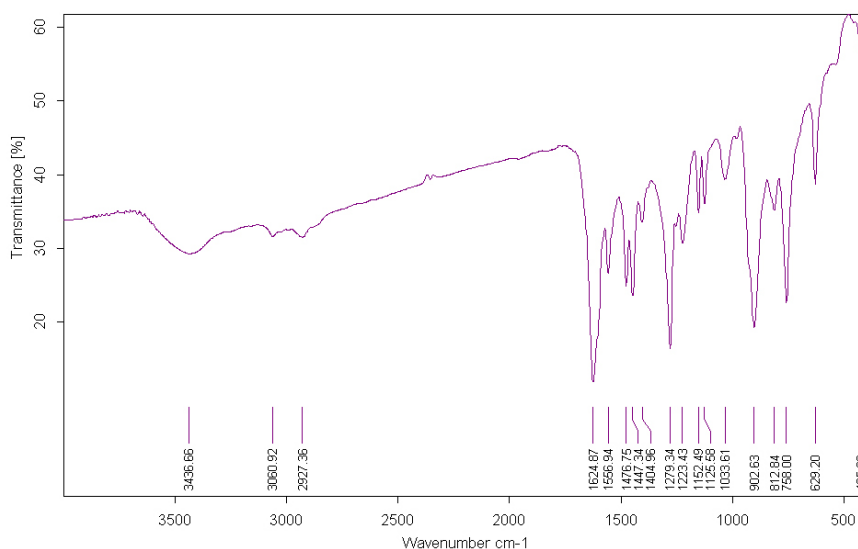
The phenolic C—O band of H<sub>2</sub>L at 1284 cm<sup>-1</sup> shifts to 1268 cm<sup>-1</sup> in Fe(III) complex and 1279 cm<sup>-1</sup> in Mo(VI) complex because of the O—M band formation (M: Fe(III) and Mo(VI)). The C=O band of H<sub>2</sub>L at 1635 cm<sup>-1</sup> shifts to 1630 cm<sup>-1</sup> in Fe(III) complex and 1625 cm<sup>-1</sup> in Mo(VI) complex and the C=N band of H<sub>2</sub>L at 1608 cm<sup>-1</sup> also shifts to 1598 cm<sup>-1</sup> in Fe(III) complex and 1557 cm<sup>-1</sup> 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 1126 cm<sup>-1</sup> and 1152 cm<sup>-1</sup> in [MoO<sub>2</sub>L] complex [18-21].



**Fig. 1.** FT-IR spectrum of the H<sub>2</sub>L dendrimer-like Schiff base ligand



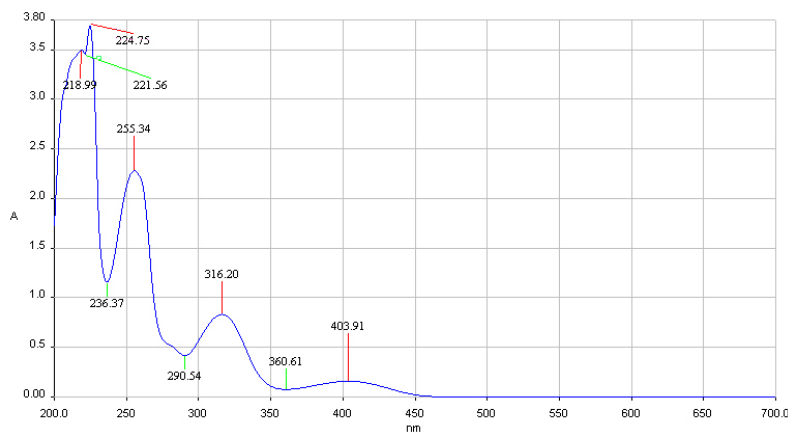
**Fig. 2.** FT-IR spectrum of [FeLCl(CH<sub>3</sub>OH)] complex



**Fig. 3.** FT-IR spectrum of  $[\text{MoO}_2\text{L}]$  complex

### 3.2. UV- Vis studies

The UV- Vis spectrum ( $>200$  nm) of  $\text{H}_2\text{L}$  in methanol consist of a band at 403.9 nm in  $\text{H}_2\text{L}$ , refer to  $n \rightarrow \pi^*$  excitation of the azomethine group and the bands appears in 225-316 nm respectively, which are assigned as  $\pi \rightarrow \pi^*$  type transitions involving molecular orbitals located on the phenolic chromophore, shift to a lower wavelength in the complexes. 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. These results show the imine group nitrogen atom has been coordinated to the metal ion. The band at 233.4 nm in  $[\text{FeLCl}(\text{CH}_3\text{OH})]$  complex refer to LMCT ( $\pi_{\text{Cl}} \rightarrow d_{\text{Fe}}$ ). [16, 22-24].

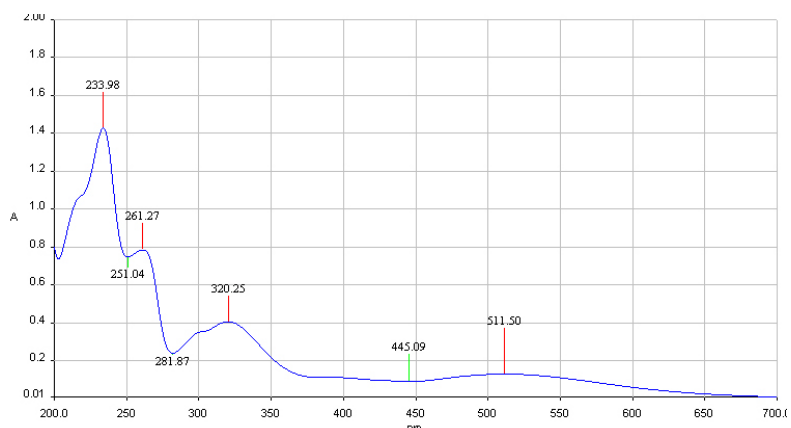


**Fig. 4.** UV-Vis spectrum of the  $\text{H}_2\text{L}$  dendrimer-like Schiff base ligand

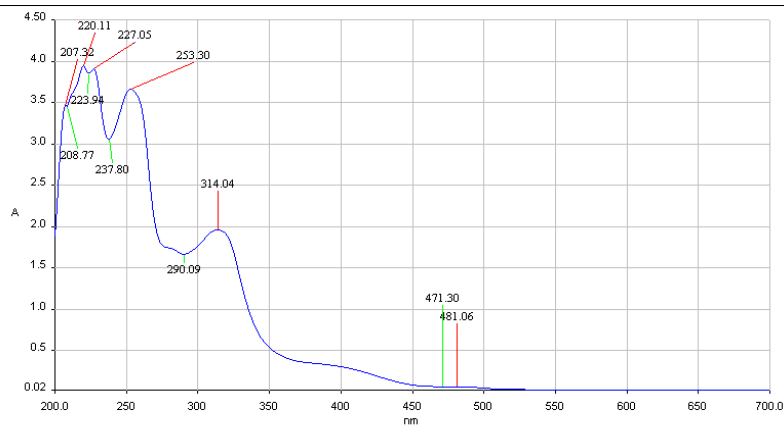
### 3.3. $^1\text{H}$ NMR studies

The  $^1\text{H}$  NMR spectrum of the Schiff base shows the presence of an azomethine and a phenolic group. Two signals that are recorded at 8.58 ppm (s, 1) and 13.38 ppm (s, 1) refers to O—H and N—H protons respectively. The aromatic protons are recorded at 6.84-7.42 ppm (m, 4). The signal that is recorded at 3.91 ppm (s, 2) refers to  $\text{CH}_2$  protons [25, 26].

The  $^{13}\text{C}$  NMR spectra of the Schiff base shows the signals at 132.142 ppm, 161.02 ppm and 167.37 ppm that are recorded for C—N, phenolic C—O and imine C=N functional groups respectively. A signal at 132.81 shows the presence of a carbonyl group in this ligand [23].

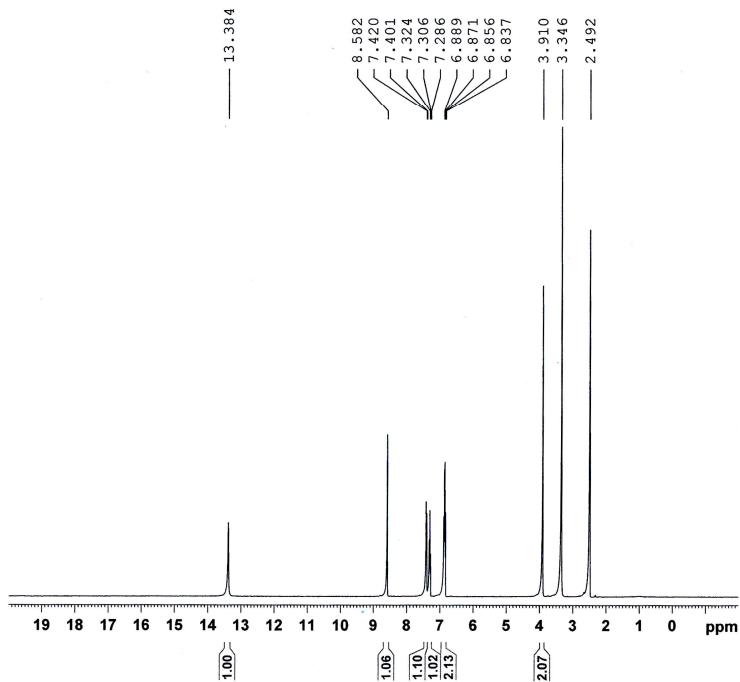


**Fig. 5.** UV-Vis spectrum of  $[\text{FeLCl}(\text{CH}_3\text{OH})]$  complex



12G91.SP

**Fig. 6.** UV-Vis spectrum of  $[\text{MoO}_2\text{L}]$  complex



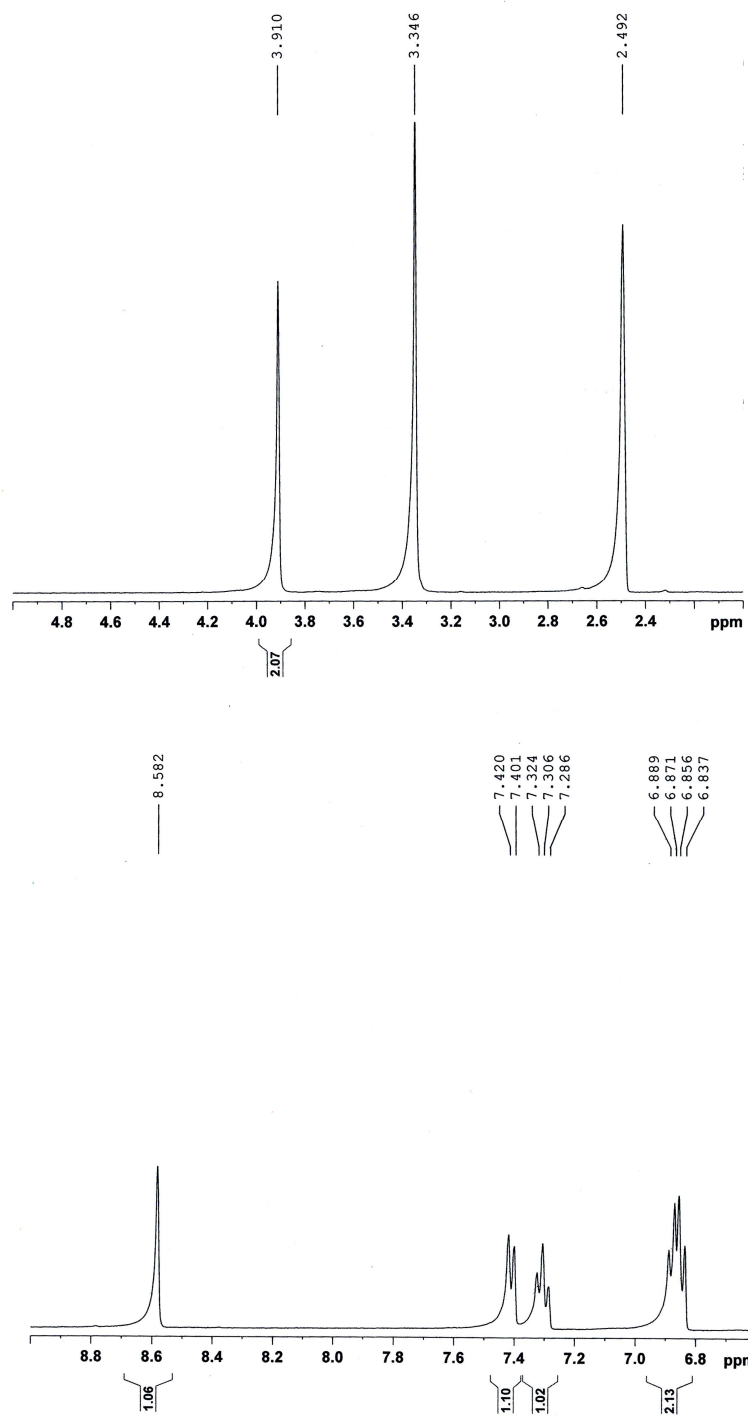


Fig. 7. <sup>1</sup>H NMR spectrum of the H<sub>2</sub>L ligand

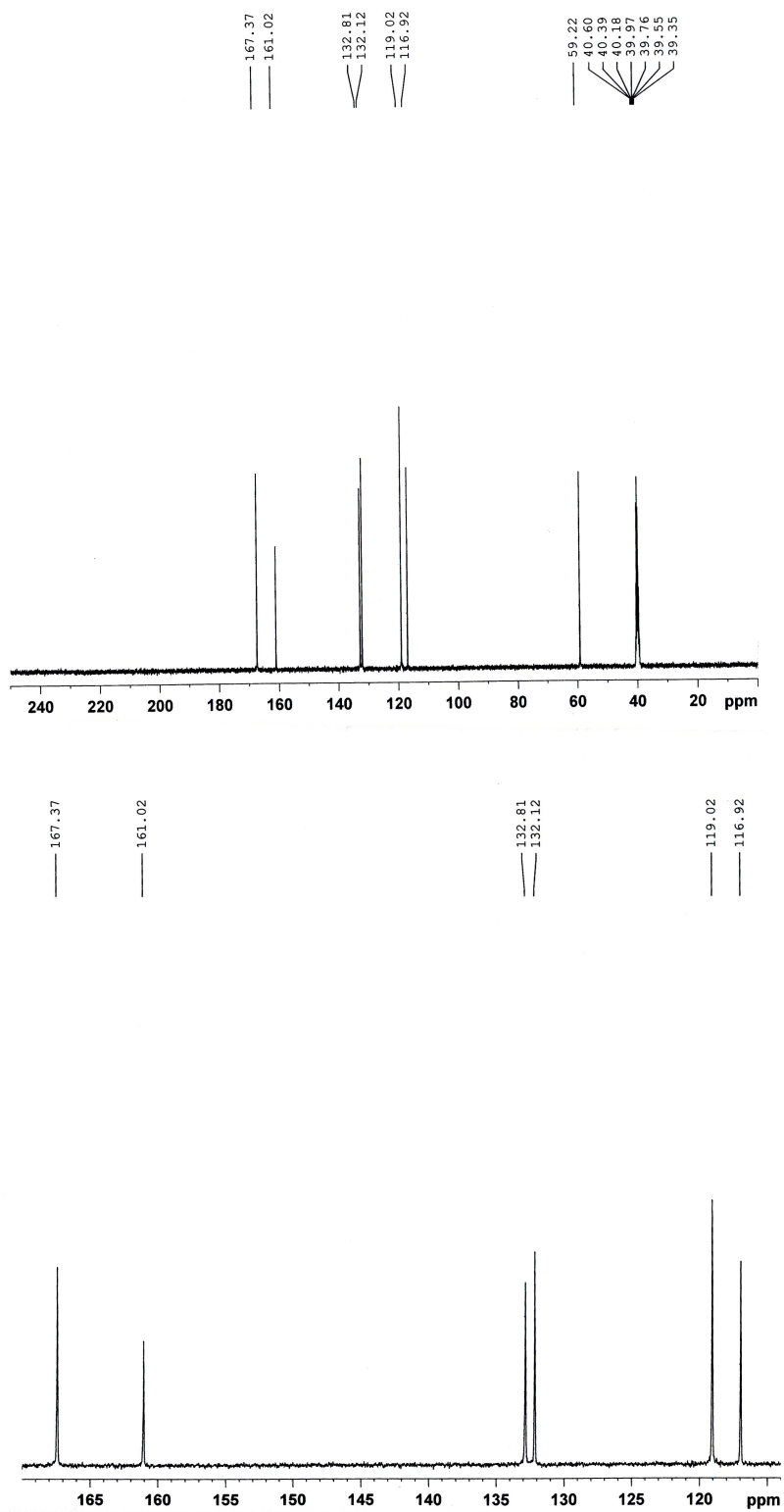


Fig. 8.  $^{13}\text{C}$  NMR spectrum of the  $\text{H}_2\text{L}$  dendrimer-like Schiff base ligand



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