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Synthesis, FT-IR and NMR characterization of new 1,3-bis(3-(2-hydroxyphenylaminomethyl)phenoxymethyl)-2,4,6-trimethylbenzene

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***Abstract*—A new ligand (L3) 1,3-bis(3-(2-hydroxyphenylaminomethyl)phenoxymethyl)-2,4,6-trimethylbenzene is synthesized. The generic synthetic pathways for the new starting materials (L_1) and (L_2) were presented. The structural features of the all the new compounds are studied by FT-IR (mid), ^{1}H and ^{13}C NMR spectroscopy. Structural comparison between (L_1) (L_2) and (L_3) were also reported.**

Keywords—Dialdehyde, Diamine, Di-imine, Diols, FT-IR, Macromolecules, NMR, spectroscopy.

I. INTRODUCTION

For many years, design and synthesis of macrohetero-multidonor ligands have constituted one of the largest areas of research in organic and coordination chemistry [1-5].

Various literatures reported the synthesis and characterization of many macromolecular compounds and there has been continuous research to explore more of the biologically important macromolecules and their respective metal complexes. In most cases, nature prefers macrocyclic derivatives for many fundamental biological functions such as photosynthesis, storage and transport of oxygen in mammalian and other respiratory systems. Schiff base macromolecules featuring di-aza compounds, peptides, esters and ethers were among the potentially active biological compounds of the recent time, and are considered among the successfully discovered macromolecular and macrocyclic compounds of great medical and biological importance [6-9].

Having various donor centres, macrocycles ligands has exciting possibilities toward construction of novel supramolecular arrangements that are capable of performing highly specific and important molecular functions. For instant, the precise molecular recognition between these macromolecular ligands and their guests, mostly transition metal ions or biomolecules (nucleic acids, proteins.), provides a good opportunity for studying key aspects of supramolecular chemistry, which are also significant in a various other disciplines such as bioorganic chemistry, biocoordination chemistry, biology, medicine and related science and technology [10-15].

The macrocyclic Schiff bases form a unique family of compartmental ligands, and modifications can be made to their basic structure such as the provision of different lateral or side chains, provision of additional donor atoms on one or more lateral chain, and partial or full saturation at the azomethine linkages. For macromolecules which have been hydrogenated or saturated at the azomethine groups, a potential donor group can
be attached on the aminic nitrogen as a pendant arm. It has been scientifically suggested that the biological and medical behaviour expressed by Schiff base macromolecules such as anticancer, antitumor, herbicidal and anti-fungal properties were attributed to the azomethine linkage in the molecules [16-20]. In this study, synthesis of macromolecular dialdehyde, diimine and their corresponding di-amines were carried out. Schiff bases of such kind have been found to be extensively useful in elaborating and determining the molecular processes occurring in biochemistry, material science, catalysis, encapsulation, activation, ion-transport and separation phenomena, hydrometallurgy, and a lot more [20-24].

II. EXPERIMENTAL

A. Chemistry

Chemicals, reagents and solvents of standard grade were used as purchased without further purification. Melting points were determined using Electro-thermal 9100 melting point apparatus. FT-IR spectra were recorded on the Bruker Alpha-P in the range of 4000-400 cm-1. Routine 1H (400 MHz) and 13C (100 MHz) spectra were recorded in DMSO-d6 or CDCl3 at ambient temperature on a Bruker Ultrashield Plus 400MHz instrument. Chemical shifts (δ) are expressed in units of parts per million relative to TMS.

The analytical and spectral data and physical properties were summarized for each experiment.

B. Synthesis

1,3-bis(3-formylphenoxymethyl)-2,4,6-trymethylbenzene (L_1).

To a solution of KOH (600 mg, 10.70 mmol) in ethanol (20 mL) was added meta-hydroxybenzaldehyde (1.20 g, 9.80 mmol) and stirred at 60oC for 45 minutes in an external oil bath. 2,4bis(chloromethyl)-1,3,5-trimethylbenzene (1.0 g, 4.60 mmol) was then added slowly at 30 minutes interval and the mixture was stirred overnight at the same temperature. The resulting product was stirred in cold distilled water, in order to remove unreacted starting materials. The purification was repeated two more times and a white solid was obtained. C25H24O4: 2.24 g, yield 80%, MP: (125-127oC ref.[34] 126-127oC). FT-IR (solid cm1): 3123 υ(C C–H), 2862 and 2760 υ(CHO), 1687 υ(C=O), 1594 υ(C C), 1217 υ(C–O), 753 δ(C C–H). 1HNMR (CDCl3), δH ppm: 2.41 (s, 6H, CH3), 2.43 (s, 3H, CH3), 5.19 (s, 4H, CH2), 7.03 (s, 1H), 7.07 (t, J = 7.53 Hz, 2H), 7.22 (d, J = 8.28 Hz, 2H), 7.61 (t, J = 7.03 Hz, 2H), 7.86 (dd, J = 7.65, 1.63 Hz, 2H), 10.39 (s, 2H, CHO). 13CNMR (CDCl3), δC ppm: 15.55 (CH3), 19.91 (2CH3), 65.54 (CH2), 112.86, 121.09, 125.23, 128.33, 130.59, 130.71, 136.03, 138.78, 138.98, 161.59, 189.73 (CHO).

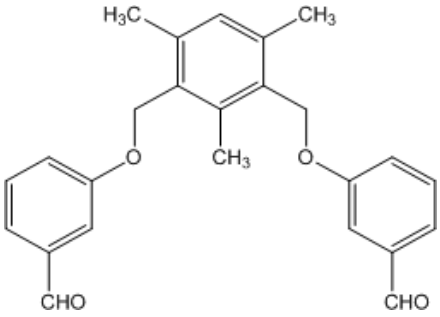

Figure 1: 1,3-bis(3-formylphenoxymethyl)-2,4,6trymethylbenzene (L_1)

1,3-bis(3-(2 hydroxyphenyliminomethyl)phenoxymethyl)2,4,6-tri-methylbenzene (L_2).

To a stirred solution of orthoaminophenol (180 mg, 1.65 mmol) in methanol (7 mL) was added ligand (L_1) (300 mg, 0.77 mmol). The reaction mixture was stirred for 3 hours at 70oC. The resulting product was cooled, filtered and cleaned two times with methanol (5 mL). A pure pale yellow solid di-imines (L2) was obtained. C37H34N2O4: 408 mg, yield 85%. Mp: 181-183oC, FT-IR: (solid, cm-1): 3336 υ(OH), 3065 υ(C C–H), 1621 υ(C=N), 1215 υ(C–O), 1590 υ(C C), 745 δ(C C–H). 1HNMR (CDCl3), δH ppm: 2.38 (s, 6H, CH3), 2.43 (s, 3H, CH3), 5.15 (s, 4H, CH2), 6.77 (td, J = 7.65, 1.25 Hz, 2H), 6.95 (d, J = 1.25 Hz, 2H), 6.97 (d, J = 1.25 Hz, 2H), 7.00 (s, 1H), 7.09 (m, 4H), 7.14 (d, J = 1.51 Hz, 2H), 7.12 (d, J = 2.76 Hz, 2H), 7.50 (t, J = 8.53, 7.28, 1.76 Hz, 2H), 8.15 (d, J = 1.76 Hz, 2H, 2CHN), 8.98 (s, 2H, OH).

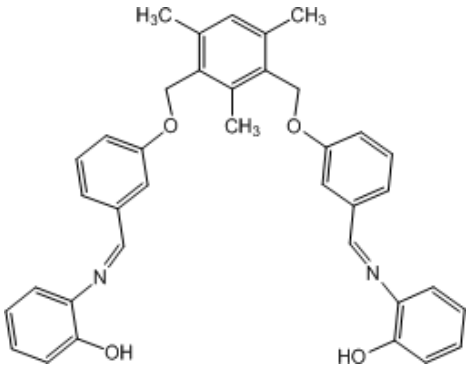

Figure 2: 1,3-bis(3-(2-hydroxyphenyliminomethyl)phenoxymethyl)-2,4,6-trimethylbenzene (L2).

1,3-bis(3-(2-hydroxyphenylaminomethyl)phenoxymethyl)2,4,6-tri-methylbenzene (L_3).

To a mixture of methanol (4 mL) and tetrahydrofuran (6 mL) was added ligand (L2) (200 mg, 0. 35 mmol) and stirred until dissolved. A solution NaBH4 (60 mg, 1.58 mmol) in methanol (1 mL) was then added slowly within 15-20 minutes at room temperature until the pale yellow colour disappeared. The reaction was then monitored by TLC until complete disappearance of starting materials was observed. The colourless solution was then precipitated in cold distilled water at pH of 5-7 and then filtered. A brown solid ligand (L3) was obtained. C37H38N2O4: 200 mg, yield 77%, MP: 68-71oC, FT-IR (solid cm-1): 3419 υ(NH), 3329 υ(OH), 3061 υ(C C–H), 1600 υ(C C), 1226 υ(C–O), 738 δ(C C–H). 1HNMR (CDCl3), δH ppm: 2.38 (s, 6H, CH3), 2.43 (s, 3H, CH3), 4.25 (s, 4H, CH2N), 5.09 (s, 4H, CH2O), 5.20 (s, 2H, NH), 6.52 (s, 1H), 6.62 (d, J = 7.53 Hz, 2H), 6.71 (d, 2 H), 6.92 (m, 2H), 7.01 ppm (m, 2H), 7.09 (d, J = 8.3 Hz, 2H), 7.24 (d, 2H), 7.28 (m, 2H). 13CNMR (CDCl3), δC ppm: 15.40 (CH3), 19.83 (2CH3), 44.55 (CH2N), 65.06 (CH2O), 111.50, 113.31, 114.44, 118.13, 120.82, 121.17, 127.99, 128.41, 129.42, 130.46, 131.16, 136.81, 138.61, 139.11, 144.41, 157.20.

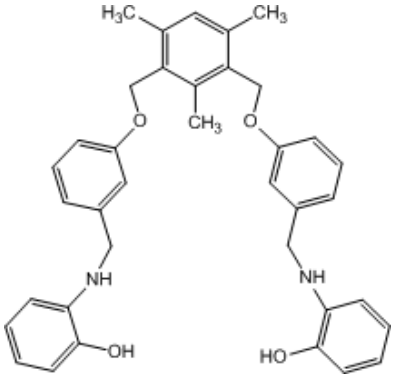

Figure 3 : 1,3-bis(3-(2-hydroxyphenylaminomethyl)phenoxymethyl)-2,4,6-trimethylbenzene (L_3).

III. RESULT AND DISCUSSION

A. FT-IR analysis

The vibrational Spectroscopy of the compounds (L1, L2 and L3) was studied in comparison so as to point out clearly the transformation of L1 via L2 to L3 there by indicating the success of the reaction pathways. For L1, the FT-IR spectrum was studied in terms of the prominent aldehydic peaks which include weak twin peaks around 2750 and 2850 cm-1 for aldehydic v(C–H), and 1685-1700 cm-1 strong for carbonyl v(C=O). The aromatic components of this ligand can be seen from 1580-1600 cm-1 for v(C C) and 700 cm-1 for δ(C C–H). In L2, the twin aldehydic hydrogen peaks disappear and a new bond around 1620-1630 cm-1 for v(CH=N) was formed. This however indicates the reaction of the aldehyde functional groups into di-imines. The peak around 3360-3370 cm1 for phenyl v(OH) usually broad also observed. All other peaks remain slightly changed. While in L3, the weak bands for v(CH=N) at 1610-1630 cm1 have disappeared due to hydrogenation of the double bonds, and a new peak between 3515cm-1 for secondary v(N–H) have been observed. The (O–H) group was observed at 3380cm-1 due to some slight changes.

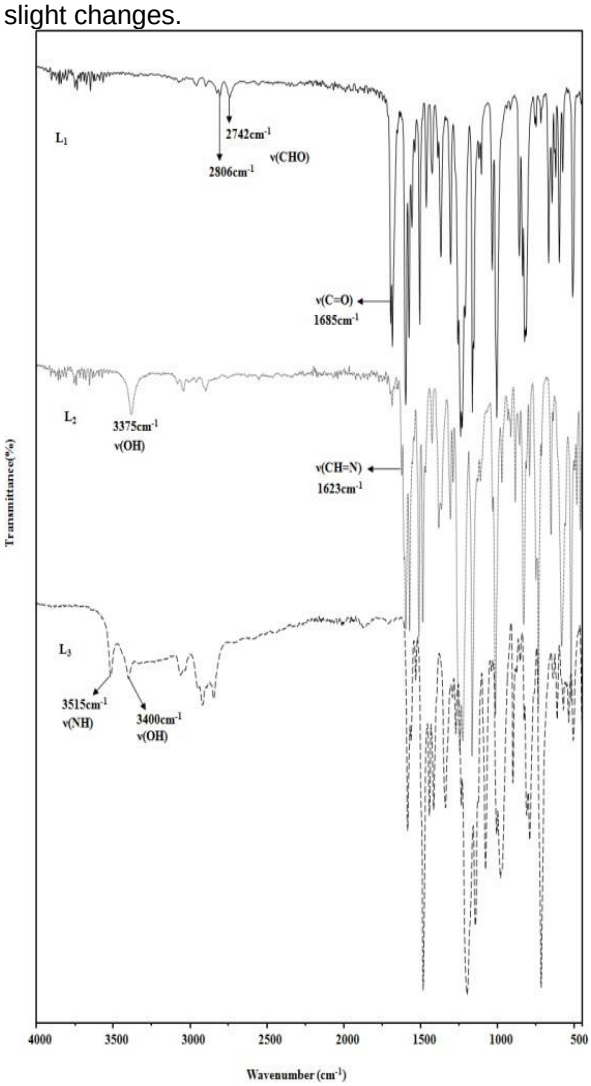

Figure 4 : Combined FT-IR Spectra of L1, L2 and L3

B. NMR anlysis

^{1}H NMR of ligand L_1 shows a singlet for ethylene (–CH2– O) protons at around 5ppm, and (CHO) protons at around 10ppm. It also shows a monomethyl (CH3) and dimethyl (2CH3) protons within the region of 2.4ppm to 2.50ppm with integrations of (3H) and (6H) respectively, belonging to the three (CH3) that are in two different magnetic environments. The (CHO) protons and the (–CH2–O) protons have integrations of (2H) and (4H) respectively. The integration for aromatic protons is significantly consistent with the structure of L_1. ^{13}C NMR of L_1 shows fourteen different carbon atoms as in the chemical structure. It also shows the monomethyl (CH3) carbon at ~ 16 ppm and dimethyl (2CH3) carbons at ~ 20 ppm. Ethylene (–CH2–O) carbons were observed around the region 6567 ppm and aldehydic (CHO) carbon at ~ 190 ppm. See figure 5

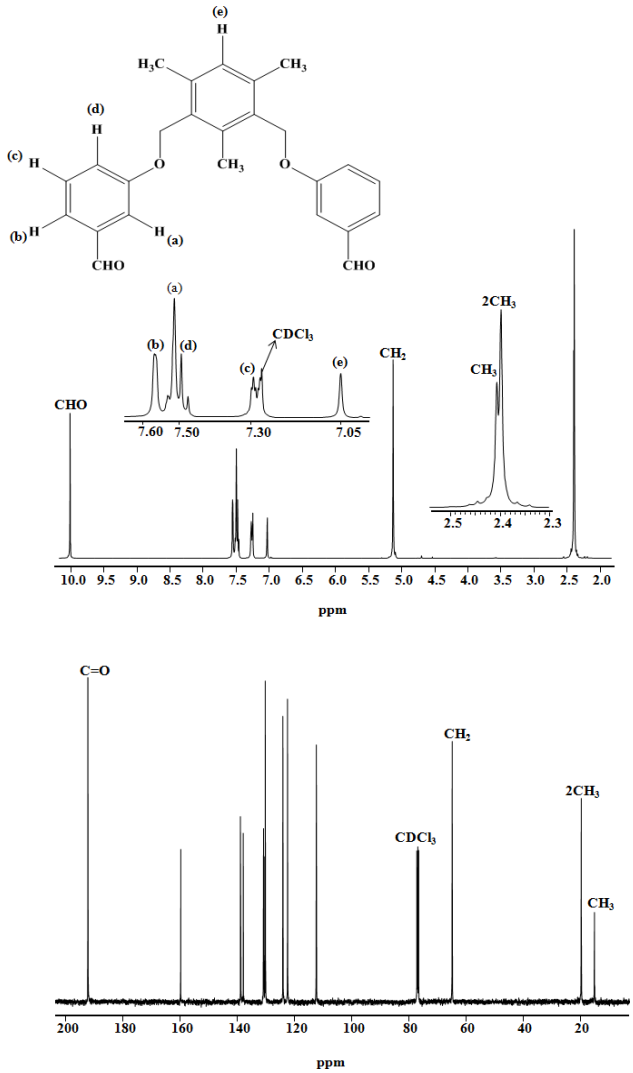

Figure 5: ^{1}H NMR and 13C NMR spectra of L1 in CDCl3.

1H NMR of L2 shows singlet for the ethylene (–CH2–O) protons still around 5.2ppm. New peaks for (HC=N) protons at ~ 7.80 ppm and (OH) protons at

around 8.70ppm were observed. The monomethyl (CH3) and dimethyl (2CH3) protons were still around 2.4 to 2.50ppm. 13C NMR of L2 show expected number of carbon atoms as in the chemical structure. The monomethyl (CH3) carbons and the dimethyl (2CH3) carbons are at 16.50 and 19.90ppm respectively. Ethylene (–CH2–O) carbons were still at 65-67ppm while the new (HC=N) carbon is at 157ppm. The complete disappearance of aldehydic (C–H) proton and aldehydic (C=O) carbon indicate the reaction have taken place between L1 and ortho-aminophenol. See figures 6.

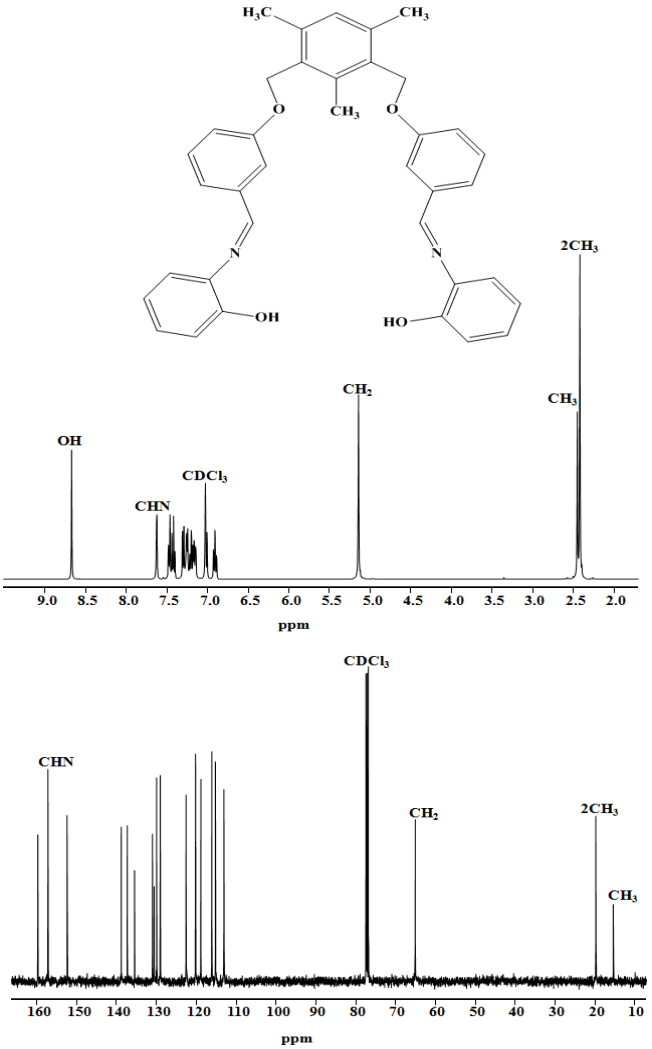

Figure 6: [1]H NMR and 13C NMR spectra L2 in CDCl3.

In L3, the peak for (HC=N) proton which was at 8.70ppm disappeared and two new peaks for (–CH2 –N) and (N–H) are subsequently observed at 4.3ppm and 5.3ppm respectively. Likewise in the 13C NMR of L3, the (HC=N) carbon at 57ppm disappeared and subsequently new (–CH2 –N) carbon appeared at 48ppm. This proves the hydrogenation of the (HC=N) double bonds into (–CH2–) and (–NH–). Unlike L1 and L2, the NMR of L3 is taken in DMSO–d6 because CDCl3 was in available in the laboratory at the time of the experiment. See figure 7.

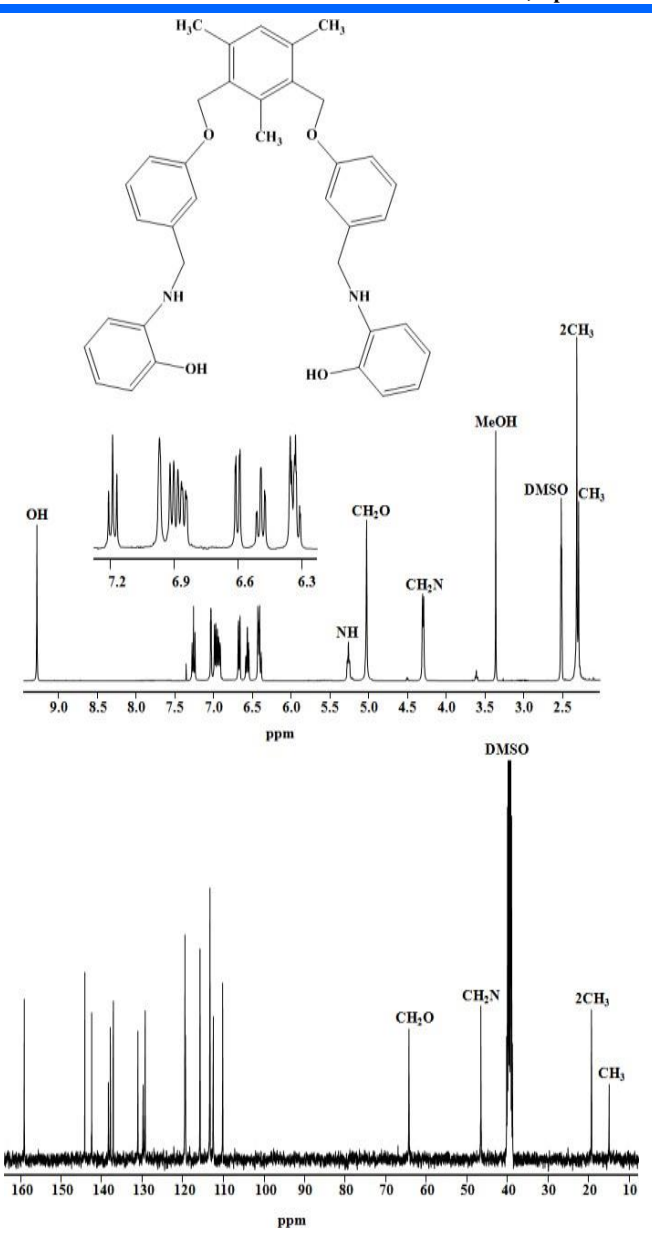

Figure 7: 1H NMR and 13C NMR spectra L3 in DMSO.

IV. CONCLUSION

Synthesis, FT-IR and NMR characterization of the new ligands have been accounted for. The synthetic steps have been carefully monitored and observed, the FT-IR and the NMR of L1, L2 and L3 have been compared in order to assure the success of the synthesis of one ligand from the other. Test on microbial and other biological activities of either the ligands alone or in metal complexes would be investigated.

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