Original Research Article

Structural Characterization Using FT-IR and NMR of Newly Synthesized 1,3-bis(3-formylphenoxymethyl)-2,4,5,6-tetrachlorobenzene and 1,3-bis(3-(2-hydroxyphenyliminomethyl)phenoxymethyl)-2,4,5,6-tetrachlorobenzene.

ABSTRACT

Aims: To synthesize a new aromatic dialdehyde using 1equivalant of 2, 4, 5, 6-tetrachloro-1,3-bis(chloromethyl)benzene and 2 equivalant of 3-hydroxybenzaldehyde. The dialdehyde obtain is to be reacted with 2 equivalant of 2-aminophenol to obtain the corresponding di-imine from the dialdehyde. Both the dialdehyde and the di-imine were to be structurally characterized by FT-IR and NMR spectroscopic study. The synthesis is to proceed to the di-imine after the dialdehyde have been structurally studied by FT-IR and NMR and confirm to have been synthesized.

Study Design: Synthesizing new macromolecular ligands using simple available starting materials and determining their chemical structure via FT-IR and NMR spectroscopy.

Place and Duration of Study: Department of Chemistry Fatih University, Istanbul, Turkey. Between January 2013 to May 2014.

Methodology: The synthesis is carried out by convectional heating method using combine heating and magnetic stirring device and a three necked reaction flask and under Argon atmosphere.

Result: Ligands were synthesized, their structures were determined and spectroscopy was carried out, presented and discussed.

Conclusion: Synthesis and structural determination of the new 1,3-bis(3-formylphenoxymethyl)-2,4,5,6-tetrachlorobenzene and 1,3-bis(3-(2-hydroxyphenyliminomethyl)phenoxymethyl)-2,4,5,6-tetrachlorobenzene ligands was successful.

Keywords: Dialdehyde, Di-imine, FT-IR, NMR, Spectroscopy.

1. INTRODUCTION

Synthesis of macromolecular ligands is regarded as one of the largest research area in coordination and organic chemistry, many of such new ligands are been discovered and there is still growing interest by many researchers to discover more [1-3].

Research in the synthesis of macromolecular and macrocyclic compounds was attributed to the fact that nature prefers such molecules for many fundamental biological functions like transport of oxygen in mammalian, photosynthesis , energy storage and respiratory systems. Di-imines (di-aza or Schiff base) were among the synthetic analogues of these macromolecular natural products synthesized to mimic their biological activities where applicable [4-9].

Modified macromolecular ligands with suitable mimicry to some important natural carrier molecules and enzymes were used in recognizing and transporting some specific metal cations, as well as understanding and reproducing the catalytic activities of metallo-enzymes [10-12]

They are also applied as chelating agents to biology and medicine as well as in chemical techniques like Magnetic Resonance Imaging (MRI) and imaging with radio isotopes and radiotherapy, due to their high kinetic and thermodynamic stability to ward release of metal ions [13].

Macrocyclic di-imine with more than one donor centres has exciting possibility toward construction of novel supramolecular arrangements that are capable of highly specific and important molecular function. A good example is the precise molecular specification and recognition between the ligands and their guest molecule which are usually the transition metals ions and biomolecule (such as nucleic acids and proteins), This provides a good opportunity for studying the key aspect of supramolecular chemistry and also significant in various other disciplines like bioorganic chemistry, biocoordination chemistry, biology and related science [14-19].

Dated back to the discovery of *cis*- platin as an antitumor agent, emphasis have been given to the preparation of coordination compounds of di-imines with suitable metal ions in both lanthanide and the transition series to produce complex compounds of desired medical and pharmaceutical importance [20-25].

Transition metal complexes of di-imine donor ligand have received much attention as catalyst in oxidation and epoxidation processes, those containing Manganese and copper centre have been prepared to study cyclic voltammetry and biological activity [26-29].

In this article, we presented the total synthesis of two new ligands (dialdehyde and its corresponding di-imine) as well as their structural characterization using both proton and carbon NMR, and Frontier Transformed Infrared Spectroscopy (FT-IR).

Convectional heating method was used in both the synthesis of the dialdehyde and the di-imine using combine heater and magnetic stirrer device. Product were analysed in their pure form, the purification was carried out in every stage of intermediary products as well as the crude product. Crude product were usually obtained in solution and had to be precipitated in pure, cold and distilled water.

The FT-IR and NMR analysis were carried out after the samples were vacuum dried at temperature lower than their melting point so as to obtain very dry samples for the structural characterization. For the NMR, ligands were found to be very soluble in both $CDCl_3$ and DMSO-d_6 and hence any of the solvents can be used for taking NMR analysis.

2. EXPERIMENTAL

2.1 Chemistry

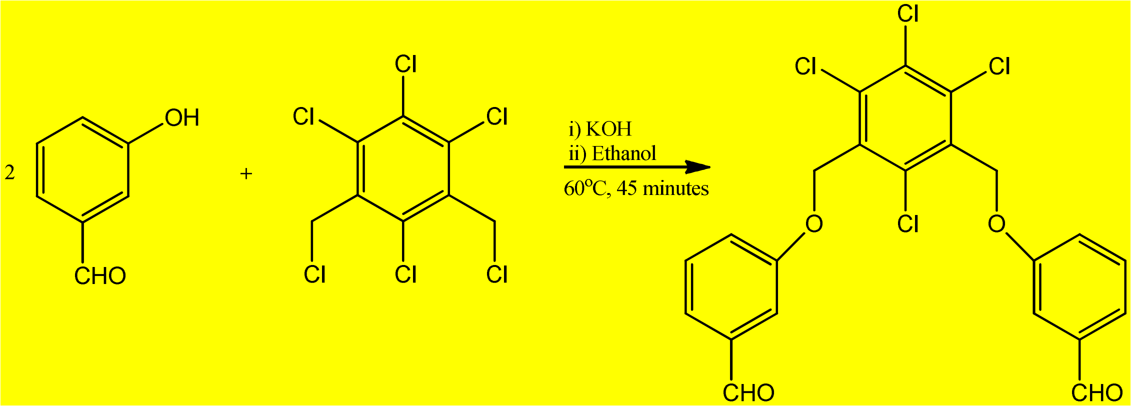
All reagents and solvents are of standard grade and were used as without purification. Electro-thermal 9100 melting point apparatus was used in determining the Melting points of the new ligands. FT-IR spectra were recorded on the Bruker Alpha-P in the range of 4000-400 cm^{-1}. Routine ^{1}H (400 MHz) and ^{13}C (100 MHz) spectra were recorded in DMSO-d_6 or $CDCl_3$ at ambient temperature on a Bruker Ultrashield Plus 400MHz instrument. Chemical shifts (δ**)** are expressed in units of parts per million relative to TMS.

2.2 Synthesis

As mentioned earlier, convectional heating method was used in both the synthesis of the dialdehyde and the di-imine using combine heater and magnetic stirrer device. The crude products were purified by washing in fresh portion of ethanol three times at room temperature, TLC was carried out and a single spot was observed which confirm the purity of the final products

<u>2.2.1 Synthesis of 1,3-bis(3-formylphenoxymethyl)-2,4,5,6-tetrachlorobenzene (Dialdehyde)</u>

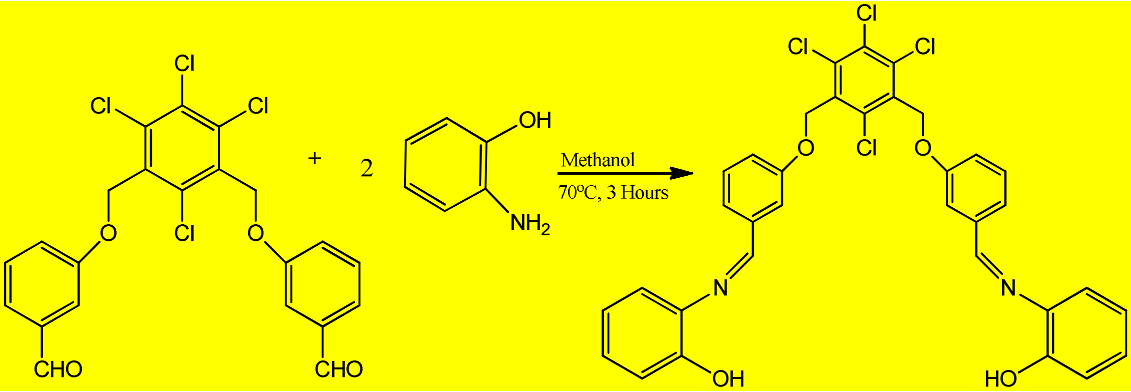
To a solution of KOH (600mg, 10.70mmol) in ethanol (20mL) was added *3*-hydroxybenzaldehyde (1.30g, 10.60mmol) and stirred at 60^{o}C for 45 minutes in an external oil bath. 2, 4, 5, 6-tetrachloro-1,3-bis(chloromethyl)benzene (1.0 g, 3.20 mmol) was then added slowly in 30 minutes interval and the mixture 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. $C_{22}H_{14}Cl_4O_4$: 1.25 g, yield 78%, MP: 172-173^{o}C. FT-IR (solid cm^{-1}): 3078 ʋ(C⎓C–H), 2820 and 2739 ʋ(CHO), 1686 ʋ(C=O), 1599 ʋ(C⎓C), 1249 ʋ(C–O), 745 δ(C⎓C–H). ^{1}HNMR ($CDCl_3$), δ_H ppm: 5.42 (s, 4H, CH_2), 7.25 (m, 2H), 7.48 (s, 2H), 7.51 (d, *J* = 8.03 Hz, 2H), 7.53 (d, *J* = 2.01 Hz, 2H), 10.01 (s, 2H, CHO). ^{13}CNMR ($CDCl_3$), δ_C ppm: 66.62 (CH_2), 112.83, 122.30, 124.52, 130.33, 132.41, 132.59, 137.06, 137.38, 137.91, 159.14, 191.93 (CHO).



Scheme. 1. Schematic synthesis of 1,3-bis(3-formylphenoxymethyl)-2,4,5,6-tetrachlorobenzene (Dialdehyde)

2.2.2 Synthesis of 1,3-bis(3-(2-hydroxyphenyliminomethyl)phenoxymethyl)-2,4,5,6-tetra-chlorobenzene (Di-imine)

To a stirred solution of *2*-aminophenol (150 mg, 1.37 mmol) in methanol (7 mL) was added the dialdehyde (synthesized in 2.2.1 above, see figure 1) (300 mg, 0.62 mmol). The reaction mixture was stirred for 3 hours at 70^{o}C. The resulting product was cooled, filtered and cleaned two times with methanol (5 mL). A pure pale yellow solid di-imines was obtained. $C_{34}H_{24}Cl_4N_2O_4$: 350 mg, yield 70%. Mp:110-111^{o}C, FT IR: (solid, cm^{-1}) 3365 ʋ(OH), 3035 ʋ(C⎓C–H), 1625 ʋ(C=N), 1587 ʋ(C⎓C), 1262 ʋ(C–O), 747 δ(C⎓C–H). ^{1}HNMR (DMSO), δ_H ppm: 5.46 (s, 4H, CH$_2$), 6.86 (t, *J* = 7.40 Hz, 2H), 6.92 (d, *J* = 7.78 Hz, 2H), 7.11 (m, 2H), 7.22 (d, *J* = 1.76 Hz, 2H), 7.25 (m, 2H), 7.48 (t, *J* = 7.91 Hz, 2H), 7.62 (d, *J* = 7.53 Hz, 2H), 7.81 (s, 2H), 8.74 (s, 2H, CHN), 9.03 (s, 2H, OH). ^{13}CNMR (DMSO), δ_C ppm: 66.51 (CH$_2$), 113.03, 116.03, 118.10, 118.78, 119.45, 123.07, 127.65, 129.91, 131.06, 133.17, 136.19, 136.73, 137.31, 138.00, 151.42, 158.55



Scheme 2. Schematic synthesis of 1,3-bis(3-(2-hydroxyphenyliminomethyl)phenoxymethyl)-2,4,5,6-tetra-chlorobenzene (Di-imine)

3. RESULT AND DISCUSSION

3.1 FT-IR Analysis

The vibrational Spectra of the dialdehyde and the di-imine were studied in comparison in order to point out clearly the synthesis of the later from the former by reacting the dialdehyde with 2-aminophenol there by indicating the success of the reaction pathways. The comparative FT-IR Spectra show the following success:

Vibrational spectroscopy of dialdehyde is studied in terms of the following important peaks: 2750-2850 cm^{-1} weak for aldehydic v(C–H) which are always two peaks. 1685-1700 cm^{-1} strong for Carbonyl v(C=O). 1580-1600 cm^{-1} strong for aromatic v(C⎓C), 1200-1250 cm^{-1} for v(C–O) and finally strong peak around 700 cm^{-1} for δ(C⎓C–H). Disappearance of strong v(O–H) vibrations of phenyl (OH) groups of hydroxybenzaldehyde within the region of 3160-3250 cm^{-1} also confirm the formation of the dialdehyde ligand. The v(C=O) of the hydroxybenzaldehyde which was at around 1673 cm^{-1} slightly shift to 1685 cm^{-1} in the dialdehyde. See figures 1.

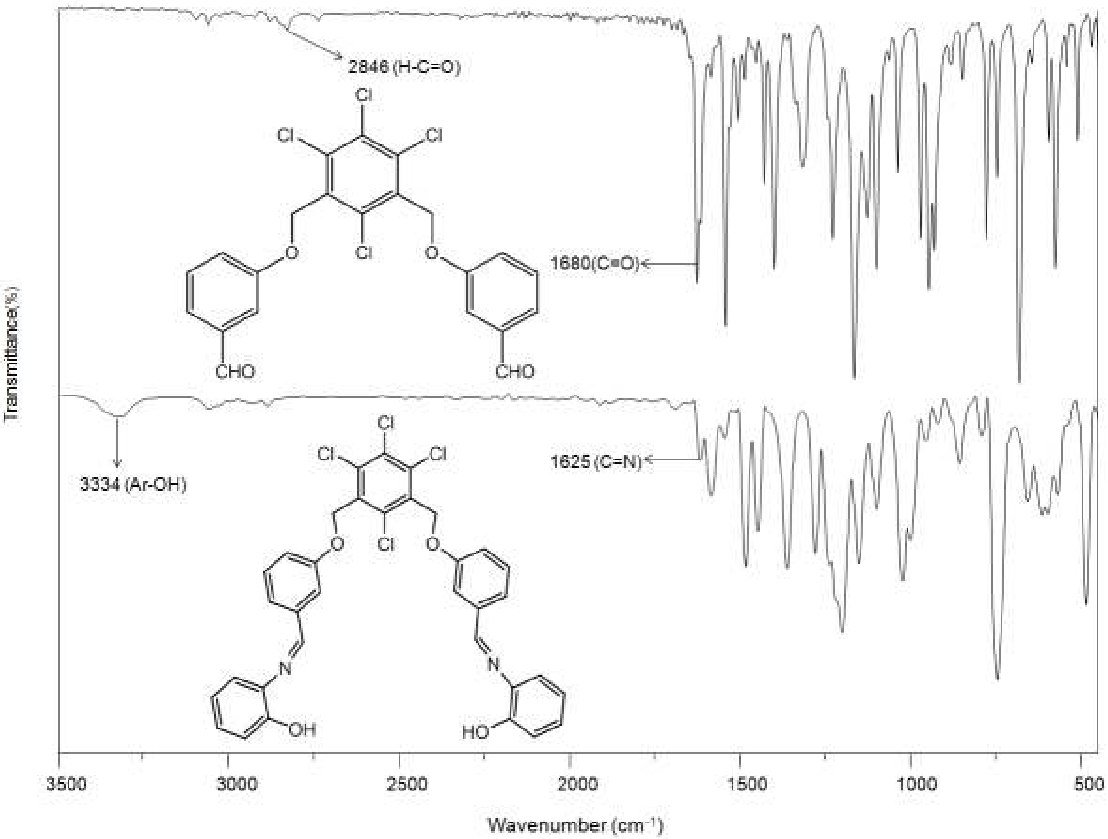


Fig. 1. Comparative FT-IR spectra of dialdehyde and di-imine

3.1 NMR Analysis

^{1}H NMR of dialdehyde shows a singlet for ethylene (CH_2) protons at around 5 - 5.20 ppm, and (CHO) protons at around 10 - 10.50 ppm. The integration for aromatic protons is significantly consistent with the structure of the dialdehyde.^{13}C NMR of the dialdehyde shows 10 different carbons atoms as expected in the chemical structure. See figure 2.

Deuterium exchange was carried out in di-imine to ascertain and differentiate the peaks for CHN and OH protons which appear in close ppm values.

^{1}H NMR of di-imines shows singlet for ethylene (CH_2) protons, around 5.2 - 5.50 ppm, and a new peak for (HC=N) protons at ~ 8.70 ppm while the (OH) protons were observed within the region of 9.00 - 9.20 ppm. ^{13}C NMR of di-imine shows 15 expected number of carbon atoms as in the chemical structure, with prominent (c=o) at around 192 ppm while the (CH_2) at around 66 ppm. See figure 3.

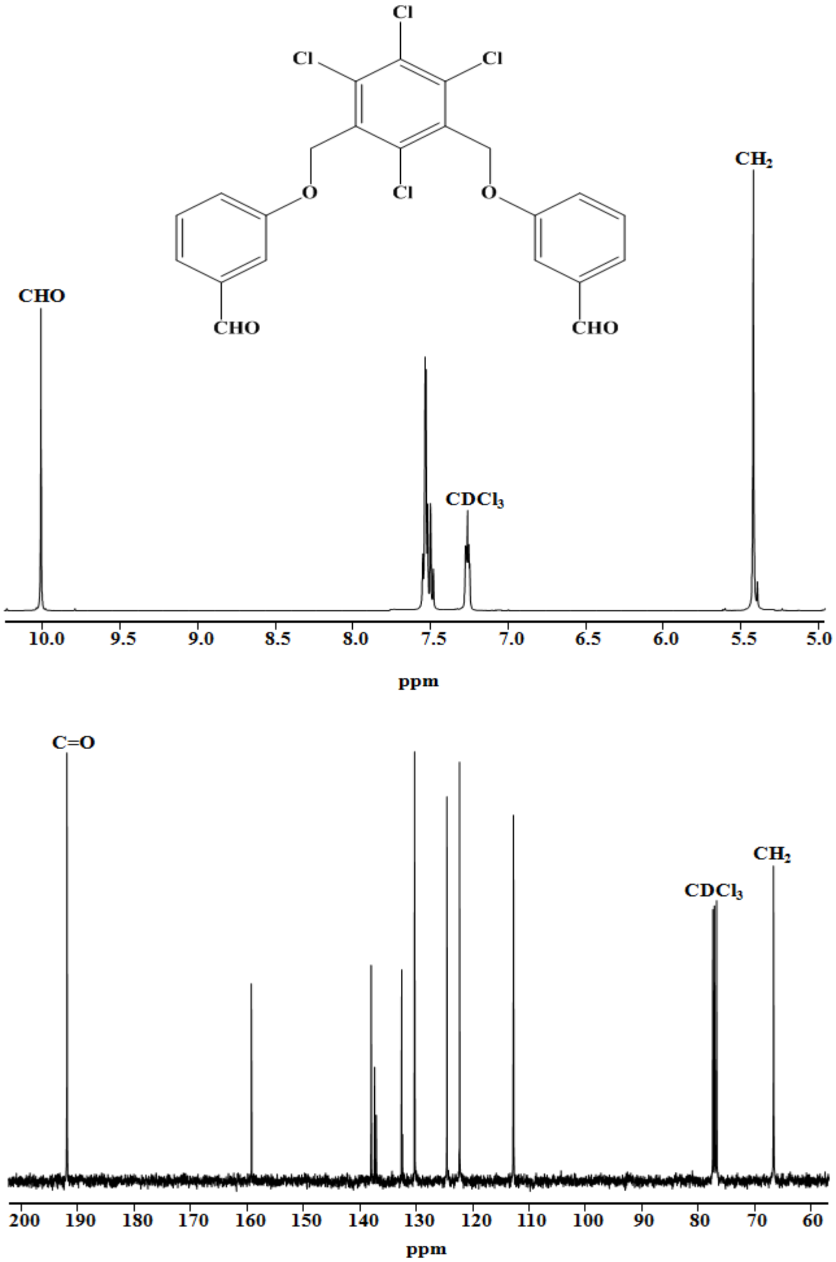


Fig. 2. ^{1}H NMR and ^{13}C NMR spectra of dialdehyde in $CDCl_3$

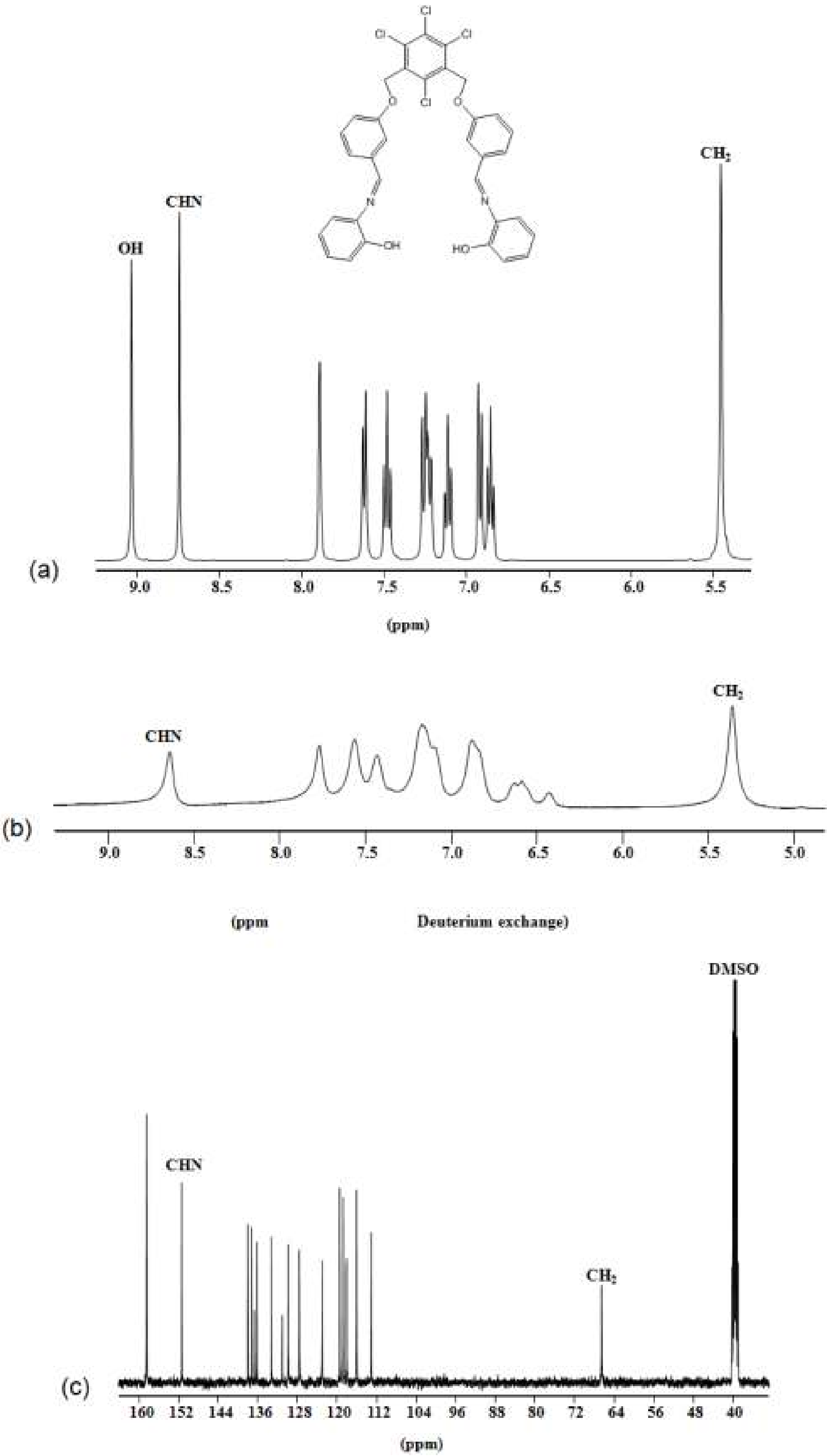


Fig. 3. ^{1}H NMR and ^{13}C NMR spectra of di-imine in CDCl$_3$

4. CONCLUSION

Structural Characterization Using FT-IR and NMR of Newly Synthesized 1,3-bis(3-formylphenoxymethyl)-2,4,5,6-tetrachlorobenzene and 1,3-bis(3-(2-hydroxyphenyliminomethyl)phenoxymethyl)-2,4,5,6-tetrachlorobenzene have been accounted for. The synthetic steps have been carefully monitored and observed. The FT-IR and the NMR of the dialdehyde and the di-imine have been compared in order to assure the success of the synthesis of one ligand from the other. All instrumental analysis were carried out using purified samples of the compounds.

REFERENCES

1. Aghatabay, M. N., Mahmiani, Y., Cevik, H., Dulger, B. Eur. J. Med. Chem. 2009;44:365–375
2. Aghatabay, M. N., Neshat, A., Karabiyik, T., Somer, M., Haciu, D., Dulger, B. Eur. J. Med. Chem. 2007;42:205.
3. Chandra, S., Gupta, L.K. Spectrochim. Acta, Part A 2004;60:1563.
4. Boojar, M.M., Shockravi, A. A. J. Med. Chem. 2007;15:3437.
5. Yi Liu, Tetrahedron Lett. 2007;48:3871.
6. Yu, S.Y., Wang, S.X., Luo, Q.H., Wang, L.F. Polyhedron1993;12:1093–1096.
7. Rekha S., Nagasundara, K.R. Indian J. Chem. A 2006;45:2421–2425.
8. Jarrahpour, A.A., Motamedifar, M., Pakshir, K., Hadi, N., Zarei, M. Molecules. 2004;9:815–824,.
9. Ramappa, P.G., Somasekharappa, K.B. Indian J. Chem. A 1994;33:66–68.
10. Guerriero, P., Tamburini, S., Vigato, P.A. *Coord. Chem. Rev.* 1995;139:17.
11. Kahn, O. in: Sikes A.G. (Ed.), *Advances in Inorganic Chemistry, Academic Press,* S. Diego, USA, 1995:179.
12. Murray, K.S. in: Sikes A.G. (Ed.), *Advanced in Inorganic Chemistry, vol. 43, Academic Press,* S. Diego, USA, 1995;261.
13. Lakshmi, B., Prabhavathi, A., Devi, M., Nagarajan, S. *J. Chem. Soc. Perkin Trans.* 1997;1495,.
14. Lakshmi, B., Prabhavathi, A., Devi, M., Nagarajan, S. J. Chem. Soc. Perkin Trans. 1997;1495.
15. Curtis, N.F. Coord. Chem. Rev. 1968;3:3.
16. Alexander, V. Chem. Rev. 1995;95:273.
17. Kahn, O. in: Sikes A.G. (Ed.), Advances in Inorganic Chemistry, Academic Press, S. Diego, USA, 1995;179.
18. Murray, K.S. in: Sikes A.G. (Ed.), Advanced in Inorganic Chemistry, vol. 43, Academic Press, S. Diego, USA, 1995;261.
19. Coper S.R. (Ed.), Crown Compounds: Toward Future Applications, VCH Publisher Inc., New York, 1992.
20. McKee, V. in: Sikes A.G. (Ed.), *Advanced in Inorganic Chemistry,* 2000;49.
21. Bandı´n, R., Bastida, R., de Blas, A., Castro, P., Fenton, D.E. Macı´as, A. Rodrı´guez, A., Rodrı´guez-Blas, T. *J. Chem. Soc., Dalton Trans.* 1994;1185.
22. R. Bastida, A. de Blas, P. Castro, D.E. Fenton, A. Macı´as, R. Rial, A. Rodrı´guez, T. Rodrı´guez-Blas, *J. Chem. Soc., Dalton Trans.* 1996;1493.
23. Adams, H., Bastida, R., de Blas, A., Carnota, M., Fenton, D.E., Macı´as, A., Rodrı´guez, A., Rodrı´guez-Blas, T. *Polyhedron* 1997;16:567.
24. Lodeiro C., Bastida, R., de Blas, A., Fenton, D.E., Macı´as, A., Rodrı´guez, A., Rodrı´guez-Blas, T. *Inorg. Chim. Acta* 1998;267:55.
25. Be´rtolo, E,. Bastida, R., de Blas, A., Fenton, D.E., Macı´as, A., Rodrı´guez, A., Rodrı´guez-Blas, T., Villar, Naturforsch., A. Z. *Teil B* 1998;53:1445.
26. R.R. Fenton, R. Gauci, P.C. Junk, L.F. Lindoy, R.C. Luckay, G.V. Meehan, J.R. Price, P. Turner, G.J. Wei, J. Chem. Soc. Dalton Trans. 2002; 2185.
27. S. Chandra, K. Gupta, Trans. Met. Chem. 2002; 27:196.
28. B.C. Gilbert, J.R.L. Smith, A.M. Payeras, J. Oakes, R.P. Prats, J. Mol. Catal. A 219 (2004) 265.
29. V. Ayala, A. Corma, M. Iglesias, F. S´anchez, J. Mol. Catal. A 2004;22:201.